THE JOURNAL OF APPLIED CHEMISTRY OF THE USSR

Vol. 24 1951

MAR

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 WEST 42ND ST. NEW YORK 18, N. Y.

—An agency for the interpretation of international knowledge—

TABLE OF CONTENTS

		page	Russ. page
1.	The processes Occuring in Dolomite when it is Calcined in the 400-1100° Range, and its use in the production of Binding Material. V. I. Shishkina and A. I. Avgustinik	247	225
2.	Accelerating the Wet Grinding of Raw Materials for Cement and Reducing the Moisture Content of the Slurry. G. K. Kukolev and L. G. Melnichenko	255	231
3.	Nonwire Porcelain Resistors with a Carbon Layer. A. I. Miklashevsky and P. I. Uspenskaya	267	242
4.	Treating Manganese Sludges and Ores with Sulfur Dioxide. V. M. Kakabadze	279	252
5.	The Fractionation of Cellulose from Cuprammonium Solutions. N. V. Shulyatikova and D. I. Mandelbaum	291	264
6.	A Comparative Evaluation of Various Methods of Preparing Trihydroxyglutaric Acid from Xylose. N. V. Chalov, O. G. Temir, Z. P. Gavrilova and A. I. Kruzhevnikova	301	274
7.	An Investigation of Some Corrosion Inhibitors. S. A. Balezin and S. K. Novikov	311	283
8.	The Effect of Solvents and Temperature upon the Copolymerization Constants of Vinyl Acetate and Monomethyl Maleate. S. N. Ushakov et al.	319	289
9.	The Effect of Slight Alkylation upon the Properties of Cellulose Fiber. N. I. Nikitin and N. I. Klenkova	327	296
10.	Changes in the Chemical and Mechanical Properties of Chlorinated Polyvinyl Chloride at High Temperatures. A. A. Berlin and I. I. Denker	339	308
11.	Using the Method of Dispersion in Anthracene Oil to Characterize the Properties of Mine and Heated Coal. V. N. Novikov	345	314
12.	Researches on Cinchona Alkaloids. N. E. Zeligson and V. V. Kolpakova	357	325
13.	The Hydrolysis of 2,6,8-Naphtholdisulfo Acid During the Sulfonation of β-Naphthol. I. I. Vorontsov	367	332
14.	The Yield of Dyestuffs in Color Development. A. I. Iordansky and G. I. Arbuzov	373	337

THE JOURNAL OF APPLIED CHEMISTRY OF THE U.S.S.R.

VOLUME XXIV, No. 3

March, 1951

Publication of the Academy of Sciences of the U. S. S. R.

IN ENGLISH TRANSLATION

Copyright, 1951

CONSULTANTS BUREAU
152 West 42 Street
New York 18, N. Y.

Printed in France

Annual Subscription $80.00, Single Copy $12.00

THE PROCESSES OCCURRING IN DOLOMITE WHEN IT IS CALCINED IN THE 400-1100° RANGE AND ITS USE IN THE PRODUCTION OF BINDING MATERIAL

V. I. Shishkina and A. I. Avgustnik

Institute of Refractories and Building Materials of the Kazakh Academy of Sciences

Most of the research done on the processes that take place in dolomite when it is calcined has been done at high temperatures (above 1300°), there being little information on the changes occurring in dolomite at low temperatures [1]. Observations on Baikonursk dolomite have enabled us to supplement this information to some extent.

The sample of Baikonursk dolomite (from Central Kazakhstan) had the following composition (%): silica 3.02; alumina 0.41; ferric oxide, 0.79; calcium oxide 30.57; magnesium oxide 20.00; sulfur trioxide 0.50; calcining losses 45.00; and moisture 0.19 (Kuzmicheva's figures). In terms of the calcined substance, these percentages are: calcium oxide 56.08; magnesium oxide 36.67; silica 7.0; free calcium oxide 47.26; and alumina and ferric oxide ratio 0.52. Inasmuch as it contains no more than 7% silica, and its calcium oxide content exceeds 19%, this material is graded as Class I metallurgical dolomite according to the All-Union Standard 10173-39.

The heating curve (8° per minute) exhibits endothermic minima at 800 and 980°; the endothermic minimum is at 610° for calcite and at 602° for magnesite [2]. The color of the material is gray; it exhibits no coarse porosity; and its structure is coarse-grained. Crystals whose faces are parallel to cleavage fissures are extremely rare. The dimensions of most of the crystals are 90-120 μ, ranging as high as 500 μ and as low as 20-60 μ. Perfect rhombohedral cleavage occurs, with the distance between the cleavage fissures 10-25 μ, xenomorphic crystals of quartz ranging in size from 20-300 μ being found, with less frequent minute sinters of limonite. Inasmuch as Baikonursk dolomite is outstanding among the dolomites we have examined (the others being Tekturmasovsk and Alexeevsk rocks) for its uniformity of grain and the definition of the crystal faces, while its composition is close to the theoretical one, it is a suitable object for investigation of pyrochemical reactions. The specific gravity of the dolomite is 2.83.

EXPERIMENTAL

Research Method. Pieces of dolomite 3-4 cm in size were calcined in crucibles placed in an electric furnace, the temperature being raised 150° per hour, with the temperature kept constant for 2 hours at 470, 500, 600, 650, 700, 750, 800, 850, 900, 980, 1000, and 1100°C.

The following quantities were measured: loss in weight (decarbonization),

volumetric shrinkage, weight by volume, apparent porosity, and absorption of water by saturation with purified kerosene for 4-6 hours in a 6-mm Hg vacuum, the experimental value being recomputed in terms of a medium with a specific gravity of one. The samples of calcined dolomite were also examined microscopically. The calculation of the areas occupied by the various phases was made by the A.A.Glagolev method, with a magnification of 40 x 8.

Moreover, the state of the magnesium oxide in the 500-800° range and its migration through the dolomite were investigated microchemically by determining the selective coloration of the magnesium oxide in the samples with an alcoholic solution of quinalizarin (tetrahydroxyanthraquinone) and microscopically.

The method of coloring the preparations was as follows: The cover glasses were removed from transparent microsections of calcined dolomite by heating them carefully over a spirit lamp. The microsection was removed and placed in an alcoholic solution of quinalizarin, to which a 2 N solution of caustic soda was added a drop at a time until the solution was bright blue or blue-violet. The section was kept in the solution for 48 hours, after which it was taken out, washed with water and with ethyl alcohol, and then affixed to a glass slide with an alcoholic solution of pine balsam and covered with a cover glass, affixed with the same balsam solution. The section was then examined under the microscope.

The calcined samples – pieces intended for immersion observations – were colored in the same way. We noted that immersion fluids containing kerosene decolorize the colored preparations.

The partial pressure of carbon dioxide was measured to obtain a direct determination of the degree of dissociation of the dolomite when heated.

This determination was made with a sample of 3 g of powder, placed in a porcelain tube, one end of which was sealed, and the other end connected to a vacuum pump with an ordinary mercury manometer connected in parallel. The tube was placed in a horizontal position in an electric furnace. Before heating began, the air was drawn out until the pressure was 10 mm hg; it was again pumped out of the system after the temperature had reached 350°; and beginning with 400°, the partial pressure of the carbon dioxide was read on the manometer at 50-degree intervals as the temperature was raised 50° per hour and kept constant for 30 minutes before each reading. When the partial pressure of carbon dioxide reached 1 atm, the gas was pumped out of the system twice, the vacuum pump was turned off, and the rise in the partial pressure was measured once more.

Three curves of the rise in partial pressure were plotted for our dolomite, as well as for Satkinsk magnesite and Kaskelensk calcite (used as standards of comparison), the mean values of these curves being taken. A correction was made for the entrance of air into the system by letting the latter cool off under vacuum, reheating, and measuring the additional pressure found in the system.

EVALUATION OF RESULTS

The determination of the decarbonization by means of the loss in weight is shown in Fig. 1.

The calcining losses (c.l.) are expressed in two ways: the usual c.l. represent the loss of weight in per cent of the initial weight of the sample (1); we also expressed the c.l. as the loss in weight in per cent of the total carbon dioxide (2). To judge by Curves 1 and 2, the dissociation process is temporarily arrested at 750-800°, building up again as the sample is heated some more, and coming to an end at 900°. This observation led us to conclude that the 750-800° range is the demarcation line between two decarbonization processes – of the magnesitic and the calcitic components.

Our observations on the increase in size and shrinkage of the dolomite (Fig. 2) indicate that the 750-800° range marks an abrupt change from shrinkage to swelling, which may be due to the termination of the decarbonization of one of the constituents and the manifestation of thermal expansion. Above 800° there sets in the decarbonization of the second constituent of the dolomite. This second process of dissociation also ought to be accompanied by shrinkage, but this latter is counteracted by the continuing thermal expansion of the material, however; on the whole, the volume of the sample does not change between 800 and 900°.

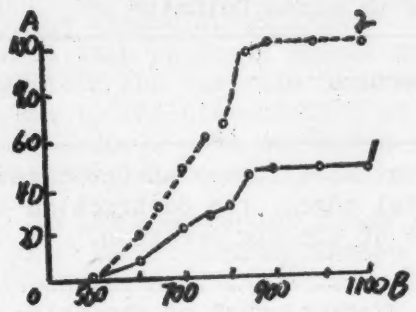


Fig. 1. Determination of decarbonization by the loss of weight during calcining.

A-Loss of weight, %; B-temperature, °C.

1-Losses during calcining, with the loss of weight expressed in % of the initial weight of the sample; 2-losses during calcining, with the loss of weight expressed in % of the total carbon dioxide.

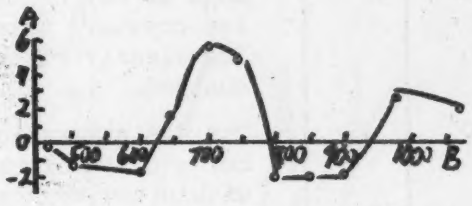


Fig. 2. Shrinkage of volume of the dolomite as a function of temperature.

A-Volumetric shrinkage, %; B-temperature, °C.

Shrinkage sets in again at higher temperatures, but this time due to different processes, as is evidenced by the data of microscopic analysis (see below), and not to decarbonization, which is practically over. In Fig. 3, the curves of volumetric weight (1), absorption of water (2), and apparent porosity (3) indicate that the respective variables reach practically constant values at 850°, which are maintained until 1000°, after which the sample is slightly condensed, due to the processes mentioned above, which have also been explored microscopically (see below).

Investigation of the partial pressures of carbon dioxide (Fig. 4) indicated that this pressure attains 760 mm at 700°C during the first stage of dissociation of dolomite, the pressure during the second stage of dissociation, after the gas had been pumped out, attaining 760 mm at approx. 930°; this supports the view that the two carbonates in dolomite behave independently.

When we compare the dissociation pressures of Satkinsk magnesite and Kaskelensk calcite (Fig. 4), we see the retarding effect of the calcareous

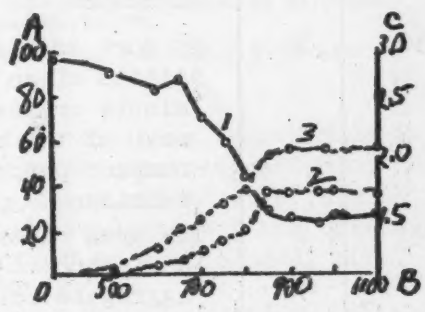


Fig. 3. Weight by volume, absorption of water, and apparent porosity of dolomite as functions of temperature.

A-Absorption of water and apparent porosity, %; B-temperature, °C.; C-weight by volume (g/cm^3).

1-Weight by volume; 2-water absorption; 3-apparent porosity.

constituent upon the dissociation of the dolomite and the closeness of the dissociation curve for this constituent to that for calcite. The results of the optical investigation of crystals of calcined dolomite are listed in Table 1.

TABLE 1

Optical Investigation of the Crystals of Calcined Dolomite

Temperature, °C	Time, hours	Nature of the microsection
470	6	Bands of a dark-gray isotropic substance appear at the cleavage fissures and along the crystal edges; the destruction affects about 10% of the surface of the microsection.
470	12	The disintegration of the crystals continues, covering as much as 20% of the microsection surface; most of the dolomite crystals take on a yellowish color, their contours being clearly visible; the limonite and the quartz are unchanged.
600	2	The disintegration affects 25% of the microsection surface, being not uniform, chiefly affecting the cleavage fissures within the crystals, 60% of which are yellowish.
600	6	The disintegration affects 62% of the microsection surface, including the portions that were colored yellow; about 17% of the dolomite is not affected.
650	2	65% of the dolomite crystals are yellowish; a new anisotropic substance (1-2%) begins to crystallize as fringes along the crystal edges of the outwardly isotropic bands of disintegrated dolomite.
650	12	The isotropic bands total 52%; the dolomite crystals have crumbled away to 0.5-0.2; the previous anisotropic bands are no longer visible.
700	2	The anisotropic substance (probably calcite) totals 10%; the isotropic bands total 25%, the spots of limonite have spread somewhat.
750	2	No more crystals of dolomite are visible; considerable quantities of an anisotropic substance, which crystallizes in minute crystals covering up to 50% of the microsection; the rest of the microsection, totaling some 40%, is covered by compact patches of calcite impregnated with an isotropic substance - probably magnesium oxide.
800	2	The area covered by the anisotropic substance with threads of an isotropic substance running through it, which exhibits aggregate polarization, is reduced to 35%.
850	6	No more anisotropic substance, practically no evidence as yet of the crystalline structure of the new phases of the material.
950	2	CaO crystallizes as minute aggregates of crystals 0.5-1.0 μ in size.
1100	2	The dimensions of the minute crystals of CaO and MgO have not been increased, a glass $\underline{N}$ = 1.560 and a slightly anisotropic material $\underline{N}$ = 1.563 making their appearance.

The data in Table 1 indicate that the dolomite is dissociated between 470 and 700° in accordance with the equation $CaCO_3 \cdot MgCO_3 \rightarrow CaCO_3 + MgO + CO_2$, which agrees with the data on the vapor pressure of the carbon dioxide.

The dissociation product is a finely-dispersed mixture, which cannot be resolved into separate phases under the microscope. The reaction begins at the edges and the cleavage fissures of the crystals. The yellowing of the crystals is due to the dissociation of extremely minute quantities of ancherite ($2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$), with oxidation of Fe^{2+} to Fe^{3+}; the impression is created that the dissociation of the ancherite accelerates the dissociation of the dolomite.

In the temperature range from 650 to 800° the following changes occur: 1) the calcite constituent recrystallizes and dissociates, starting at about 750°; and 2) the magnesium oxide migrates into the finely dispersed bodies, occupying the place of the former dolomite crystals, giving rise to areas of amorphous magnesium oxide, visible as dark patches. The details of this process were investigated separately by coloring with quinalizarin (see below).

At higher temperatures the underlying dissociation of the calcite takes place, being completed at about 930°; this agrees with the data on dissociation pressure. A glass phase with a $\underline{N} = 1.560$ is found to exist at 1100°.

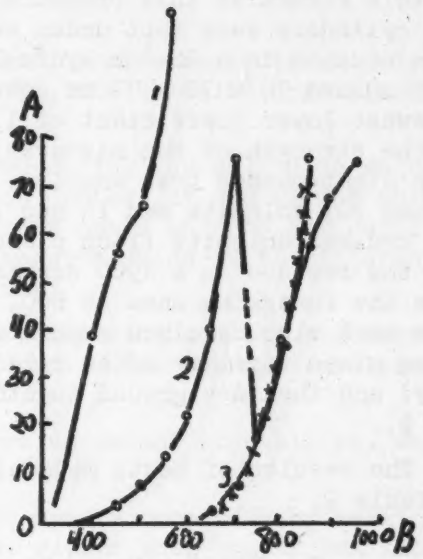


Fig. 4. Dissociation pressure of Satkinsk magnesite, Kaskelensk calcite, and Baikonursk dolomite.

A-Dissociation pressure, mm Hg column; B-temperature, °C.

1-Magnesite; 2-dolomite; 3-calcite.

Treating the microsections with a solution of quinalizarin, which colored them blue by reacting with the Mg^{2+} ions, yielded the following results: a) the areas where an amorphous substance was formed at lower temperatures (600°) was colored blue where it was in contact with quartz; hence, quartz accelerates the dissociation of dolomite; b) as the calcining temperature is raised, all of the isomorphic substance produced by the disintegration of the dolomite is colored; we find that the dolomite is also colored, the intensity of the color diminishing from the periphery toward the center of the crystals; and c) the anisotropic substance that appears at 700° is not colored, thus proving its calcitic nature.

This coloring method likewise confirmed the notion that free magnesium oxide is formed above 500° as a result of the reaction: $CaCO_3 \cdot MgCO_3 \rightarrow CaCO_3 + MgO + CO_2$, which is more vigorous at the crystal edges and along the cleavage fissures.

We tested the binding properties of dolomite at low calcining temperatures.

Aisitomarsk kaolin clay (47.01% silica, 38.36% alumina, 0.88% ferric oxide, traces of calcium and magnesium oxides, 12.78% losses in calcining, 0.42% hygroscopicity) was used as the other constituent of the mixture. We compared the binding properties of Baikonursk dolomite by itself with those of a mixture

of the dolomite with Aisitomarsk clay. All the comparable research samples were calcined in an electric furnace under identical conditions at 600, 700, and 800°C.

The dolomite was pulverized by dry grinding in a ball mill until the residue on a 4900 screen (with 4900 openings per cm^2) totaled 3-4%. The powder was calcined in a fire-clay box, being held at one of the foregoing temperatures for one hour. The binding properties of the calcined dolomite were determined in accordance with Government Standard 2542-44 and by the Minas method, in a 1:3 mixture with washed Alma-Ata sand (fraction that passes through screens with 250 to 900 openings per sq cm), using enough mixing water so that no water was forced out of the solution at a pressure of 100 kg/cm^2. Cylinders 28 x 28 mm were formed at this pressure, being kept at the pressure for 10 seconds. The cylinders were kept under water for 7 days at room temperature, and then were crushed in a 20-ton hydraulic press. Recomputation of the results in terms of standard 70 x 70 x 70 mm cubes was effected by multiplying the results by a somewhat lower coefficient of 1.5, which ought to guard against an exaggeration of the strength of the mixtures. The Government Standard 2542-44 test was made with eight-shaped test samples, prepared from the same mixture. Mixtures of 85 and 90% dolomite and 15 and 10% clay, respectively, were prepared by grinding crushed dolomite (1-cm pieces) together with dried clay in a ball mill until the residue on a 4900 screen totaled 3-4%. These mixtures were calcined like the foregoing ones at 600, 700, and 800°. Moreover, the clay and the dolomite were also calcined separately, in 2-3 cm pieces, under the same conditions, being mixed together after calcining in the specified proportions (15 and 20% clay) and then dry-ground together until the residue on a 4900 screen totaled 3-4 %.

The results of tests made after 7 days of storage under water are listed in Table 2.

TABLE 2

The Binding Properties of Dolomite and a Dolomite-Clay Mixture

Mixture and component ratio	Calcining temp., °C	Mixing water, %	Setting time, hrs and minutes	Compression strength, kg/cm^2	Tensile strength, kg/cm^2	Hydraulicity
Dolomite and sand, 1:3....	600	33	5-	2.3	0.05	Non-hydraulic
	700	41.7	6-05	4.1	3.1	Non-hydraulic
	800	50.0	5-13	13.3	5.0	Non-hydraulic
Dolomite and clay dry-ground together and calcined 90:10	600	43.3	2-47	40.4	0.5	Non-hydraulic
	700	48.3	3-15	59.7	4.66	Non-hydraulic
	800	60.0	4-20	41.6	5.1	Hydraulic
Ditto, 85:15	600	43.3	1-15	40.3	7.3	Hydraulic
	700	45.0	2-40	41.3	7.7	Hydraulic
	800	41.6	1-40	16.9	5.1	Hydraulic
Dolomite and clay calcined separately and ground together, 85:15	600	40.0	8-40	33.5	-	Non-hydraulic
	700	51.7	7-30	66.2	-	Non-hydraulic
	800	63.0	8-27	62.5	-	Hydraulic
Ditto, 80:20	600	41.6	-45	33.5	6.5	Hydraulic
	700	42.6	-25	45.2	4.7	Hydraulic
	800	38.8	-50	24.1	5.1	Hydraulic

We see in Table 2 that adding clay appreciably increases the strength of the binding material, besides conferring hydraulic properties upon it. The optimum strength is attained with separate calcining of the clay and the dolomite at 700°, after which they are mixed together; calcining at 800° lowers the strength in every instance. This fact indicates that the principal factor responsible for the manifestation of binding properties under the specified calcining conditions (up to 800°) is magnesium oxide, the 600-700° range being the optimum temperature for the latter's formation.

Microscopic examination of the quartz grains in the calcined mixtures revealed that they had undergone no change as a result of interaction with the magnesium oxide (apparently owing to the large grain size of the quartz).

SUMMARY

1. Baikonursk dolomite is dissociated in the 470-700°C range in accordance with the equation $CaCO_3 \cdot MgCO_3 \rightarrow CaCO_3 + MgO + CO_2$, the dolomite crystals disintegrating as the calcining progresses.

2. In the 650-800° range, the calcite evolved during the calcining recrystallizes, and the magnesium oxide migrates to the centers of the former dolomite crystals, forming compact patches. As this process nears an end, the calcite crystallizes in layers with finely dispersed magnesium oxide in the interiors of the former dolomite grains. The sample shrinks.

3. In the 750-900° range, the calcite is decarbonized, and the structure formed when the calcite crystallized is broken down. This process involves an increase in the dimensions of the sample.

4. In the 850-1100° range, calcium and magnesium oxides crystallize, while the density of the material rises somewhat.

5. Decarbonized dolomite is suitable for the manufacture of a hydraulic cement, due to the formation of magnesium oxide, either when ground and calcined together with kaolin clay at low temperatures (optimum at about 700° C) or calcined separately and ground together. Its compression strength after storage for seven days is of the order of 66 kg/cm^2.

LITERATURE CITED

[1] P.P.Budnikov and A.S.Berezhnoi, Prog.Chem., 15, 5, 521 (1949); S.I. Kilesso, Refractories Handbook II, 612 (1939); A.A.Baikov, The Physical and Chemical Conditions Governing the Manufacture of Refractories, Proc. Acad. Sci. USSR (1931); G.K.Butkevich. Caustic Dolomite. Technical Press (1933).

[2] L.G.Berg, A.V.Nikolaev, and E.A.Rode. Thermography. USSR Acad.Sci. Press (1948).

Received September 5, 1950.

ACCELERATING THE WET GRINDING OF RAW MATERIALS FOR CEMENT AND REDUCING THE MOISTURE CONTENT OF THE SLURRY

G. V. Kukolev and L. G. Melnichenko

In the production of Portland cement by the wet method, using comparatively unstable raw materials, reducing the moisture in the slurries, and speeding up the wet dispersion or "running" of the materials are essential.

Of the many methods employed to reduce the moisture in the slurries, which is as high as 50% in some instances, special additives – diluents – are most desirable for this purpose.

Such substances increase the fluidity of the slurry for a given moisture content. Most of the research on this topic has been done in the Soviet Union. Budnikov, Kukolev, and Lezhoev, [1], for instance, have made a laboratory study of the effect of adding sodium hydroxide, soda, water glass, syrups, and mixtures of these substances upon the fluidity of high-moisture slurries of raw materials used at the Amvrosievsk plant. The authors' results indicate that the diluting effect of these electrolytes diminishes in the following order: water glass, soda, and sodium hydroxide. Moreover, the diluents evince greater activity in more viscous slurries, the dilution effect depending largely upon the concentration of the additive, attaining a maximum for a definite concentration of each reagent and depending upon the nature of the raw material and its content of water-soluble salts. Syrup, and especially a soda-syrup mixture, proved to be the best diluents in these experiments. Introducing these additives made it possible to lower the moisture content of the slurry by about 5% without affecting its fluidity.

Kevesh has made a comprehensive study of the effect of sodium hydroxide upon reducing the moisture content of slurry at the Shurovka cement plant, first on a laboratory scale and then under factory conditions [2]. Maximum liquefaction, ensuring a lowering of the slurry moisture content by 5%, was obtained when the sodium hydroxide totaled 0.33% by weight of the dry sludge.

Tovarov [3] cites the results of experiments he ran to determine the effect of sulfite-cellulose lye and lime upon the fluidity of a clayey-limestone slurry. Adding 0.5% of lime to the slurry increased the latter's viscosity, though sulfite-cellulose lye liquefied the slurry considerably; adding 0.5% of the lye made it possible to reduce the moisture content by about 4%. A check of these results at the "Bolshevik" plant confirmed the laboratory figures.

In addition, it has been found that surface-active substances exert a strong liquefying effect on the wet grinding of some materials in laboratory ball mills, using water, kerosene, toluene, and other media, and that the nature of the reagent's action upon the viscosity of the suspension is related to its stabilizing (peptizing) activity [4].

On the other hand, Rebinder and his associates [4] have shown in their numerous researches that the wet dispersion of solids can be accelerated by the introduction of certain additives (in drilling wells, treatment of metals, grinding in ball mills, etc.). Many such additives – which reduce hardness – likewise act as stabilizers of the suspensions of these materials. Mineral and organic substances, as true or colloidal solutions, may serve as additives of this sort.

The foregoing processes are founded upon adsorption phenomena that occur at the solid – liquid boundary. The properties of an electrical double layer in the case of electrolytes and of an adsorption – solvate molecular layer in the case of molecular and colloidal solutions are of fundamental importance in this connection.

In the paper referred to above, Budnikov, Kukolev, and Lezhoev [1] conducted comparative wet grinding of marl and chalk in the Amvrosievsk cement plant in two laboratory ball mills, using a water medium and adding a mixture consisting of 0.1% syrup by weight of the slurry and a 0.04 N soda solution. After grinding, they subjected the materials to screen analysis and levigation of the slurry. The powder containing the specified diluents had about 20% less of the coarse fractions than the powder ground in pure water.

Other authors have commented on the appreciable acceleration of dispersion achieved with various materials by introducing additives (clay plus water glass, andalusite and graphite with sulfite-cellulose lye, emery plus soda, etc.).

The authors of the present paper have found that the introduction of the optimum additives resulted in an acceleration of 30-40% in the wet grinding of carbonates and quartzes in ball mills, under laboraotry conditions and in pilot plants.

The present paper reports on the effect of various additives upon the speeding up of the wet dispersing of Podgornensk marl and on the liquefaction of slurries of this marl, of Belgorod chalk, of Glukhovetsk kaolin, and of the slurry of the Amvrosievsk cement plant.

Podgorensk marl is a soft clayey rock, sometimes containing leaflets of muscovite, minute grains of quartz, ferric oxide, and calcium carbonate, distributed nearly uniformly throughout the rock. The marl had the following composition: 34.2% SiO_2; 5.96% R_2O_3; 31.88% CaO; 0.83% MgO; 26.56 losses in calcining; total 99.43%. The other materials are fairly well known, and we need not list their composition here.

Both inorganic and organic reagents, as well as their mixtures, were used as additives in our research.

EXPERIMENTAL

The specified marl was wet ground in 2-liter porcelain ball mills at an r.p.m. that was 80% of the critical speed, the proportions of the weights of the balls, the material, and the water being B:M:W = 1.7:1.0:0.8. The resulting moisture content of the pulp was 45%. Before grinding, the marl was screened into the following fractions: -3.0 + 1.5 mm; -1.5 + 0.5 mm; -0.5 + 0.2 mm.

Grinding lasted 10 to 15 minutes. The grind product – the slurry – was subjected to wet and dry screen analysis on screens with 900, 4900, and 10,000 openings per cm^2. The efficiency (the acceleration of the grinding process) was determined by the decrease in the total residue left on the 4900 and 10,000 screens after grinding with additives as compared to the residues left on the same screens with grinding in water alone. The efficiency was expressed in per cent: (+) signifying acceleration and (-) signifying retardation. The efficiency

values cited are the mean of no less than three similar grinds. Both distilled and tap water were used; the hardness of the latter was as follows: 15° total hardness and 9° temporary hardness; and its chlorine-ion content was 24 mg per liter (except in the slurry of the Amvrosievsk cement plant).

The results of our investigations of the effect of adding electrolytes, nonelectrolytes, and mixtures of the two upon grinding in distilled and tap water are given in Tables 1, 2, and 3; the variation of efficiency with the concentration of the electrolytes is shown in Fig. 1.

TABLE 1

Effect of Mineral Additives Upon the Wet Grinding of Marl (in Distilled Water)

Name of additive (electrolytes)	Optimum concentration of additive, %	Efficiency, % of residue		Remarks
		On a 4900 screen	On a 10,000 screen	
Sodium hydroxide	0.20	+30	+26	Initial fraction:
Lime solution	0.1	-16	- 4	-1.5 + 0.5 mm
Soda	0.25	+42	+23	B:M:W = 1.7:1.0:
Water glass	0.04	+16	+12	1.8
Soda-water glass mixture	0.04	+40	+22	Moisture 44%;
Table salt	0.3	0	0	Duration of grind-
Soda-table salt mixture	0.3 - 0.5	+10	+10	ing 15 minutes
Hydrochloric acid	1.2	+40	+22	
Saturation with carbon dioxide for 10 minutes at 18° C	-	+45	+28	

We see from Table 1 that in most cases the dispersing of marl takes place faster when an electrolyte is present than in water alone; caustic soda and alkaline salts that undergo hydrolysis speed up the running of the material considerably. Soda is most active in this respect, followed by sodium hydroxide and then by water glass. As we see from Fig. 1, the accelerating effect of electrolytes depends largely on the concentration of the additive. The curves for soda (2) and for water glass (3) exhibit a maximum, on either side of which the acceleration of grinding drops off, whereas an increase in the concentration of water glass actually slows down grinding. We may therefore speak of an optimum concentration of additive in these instances. A soda-water glass mixture likewise has a favorable effect. Sodium chloride does not act at all, while it speeds up grinding less when mixed with soda than soda does all by itself in similar concentration. A saturated solution of lime retards the grinding of marl. Acids, both hydrochloric and carbonic, greatly accelerate the rate of grinding. Thus, electrolytes exert a selective effect upon the acceleration of the rate of grinding of marl, their action varying with their concentration.

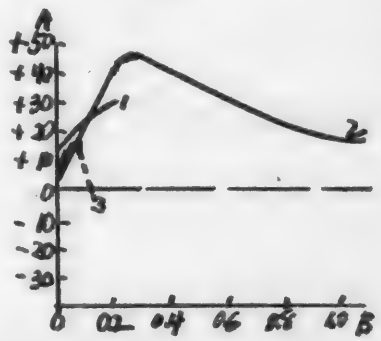


Fig. 1. Grinding efficiency as a function of electrolyte concentration.

A-Grinding efficiency, % B-% electrolyte.

1-NaOH; 2-Na_2CO_3; 3-$Na_2O \cdot n SiO_2$.

As is seen in Table 2, the effect of organic additives and of mixtures of the latter with alkaline electrolytes is always positive and appreciable with syrup, sulfite-cellulose lye, and peat extract in water glass. This effect is somewhat less marked when grinding is done with soap or peat extract in caustic soda.

TABLE 2

Effect of Organic Additives and Mixtures

Name of additive (nonelectrolytes and mixtures)	Optimum concentration of additive, %	Efficiency, % residue	
		On a 4900 screen	On a 10,000 screen
Syrup	1.2	+37	+11
Sulfite-cellulose lye	1.2	+25	+ 6
Potash soap	0.4	+18	+16
Peat extract in caustic soda ..	0.008 (in terms of Na_2O)	+8	+15
Ditto in water glass	0.12	+17	+23
Soda-syrup mixture	0.5 and 1.0	–	+20

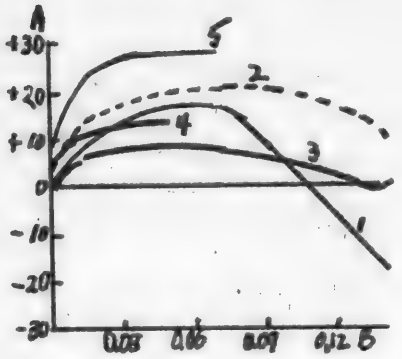


Fig. 2. Fluidity as a function of reagent concentration.

A-% change of fluidity; B-% reagent (by weight of solid).

1-NaOH; 2-Na_2CO_3; 3-$Na_2O \cdot nSiO_2$; 4-peat extract in waterglass; 5-peat extract in NaOH.

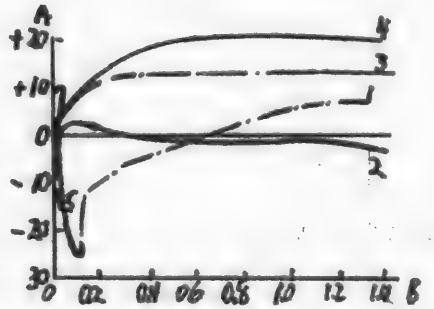


Fig. 3. Fluidity as a function of reagent concentration.

A-% change of fluidity; B-% reagent (by weight of solid).

1-Syrup in distilled water; 2-syrup in tap water; 3-sulfite-cellulose lye in distilled water; 4-sulfite-cellulose lye in tap water; 5-soap.

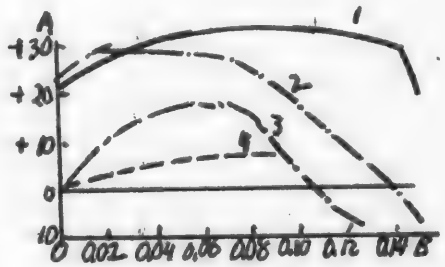


Fig. 4. Fluidity as a function of reagent concentration.

A-% change of fluidity; B-% reagent (by weight of solid).

1-1.4% sulfite-cellulose lye + NaOH in tap water; 2-sulfite cellulose lye + NaOH in distilled water; 3-NaOH in distilled water; 4-sulfite-cellulose lye in distilled water.

Inasmuch as marl consists of carbonate and argillaceous substances in a finely dispersed state, any dispersing agent whose action is generally positive upon one of the constituents of marl will speed up the rate of grinding for the marl as a whole.

The best results will obviously be obtained when the reagents act positively upon both the calcareous and the argillaceous constituents of the marl. This is found to be actually the case, as the subjoined figures prove.

The effect of some of the most active accelerators of the grinding of marl in tap water is given in Table 3.

According to Rebinder [4], the mineral content of water may affect the activity of anti-hardness agents considerably; in some cases, depending upon the nature of the material and of the ions contained in the water, the effect of an additive upon the grinding rate may be weakened or canceled out entirely.

TABLE 3

Acceleration of Wet Grinding of Marl (In Tap Water)

Additive	Optimum concentration, %	Efficiency, per cent residue	
		On a 4900 screen	On a 10,000 screen
Soda	0.25	+10	+16
Soda-water glass mixt..	0.2 and 0.08	+ 5	+ 8
Sulfite-cellulose-lye-soda mixt...	1.0 and 0.2	+27	+37

It follows from Table 3, as well as from the rest of our data, that the positive action of the best additives is conserved when we shift from distilled water to tap water, though the absolute value of the effect is often diminished, being attained only at relatively high concentrations, which testifies to the possibility that part of the reagent may be lost as a result of its reacting with the salts contained in such water. A very significant effect was achieved with a soda-sulfite-cellulose lye mixture in grinding with tap water. Thus, the addition of a small quantity of soda or of a mixture of soda and sulfite-cellulose lye, or of peat or lignite extracts, can speed up the wet dispersing, the "running", of marl considerably.

Recalculation of the results we attained in speeding up the rate of grinding showed that this method yields an increase of 25 to 30% in the output of the grinding apparatus (the mill).

Effect of reagents upon the fluidity of the slurry. The effect of several reagents upon fluidity was tested with slurries of marl, chalk, kaolin in distilled and tap water, prepared under laboratory conditions, as well as with the slurry of the Amvrosievsk cement plant.

The fluidity of the slurry was determined by the gravimetric or volumetric method in a specially designed glass tube drawn out at one end. In the volumetric method, the time required for 100 cm^3 of the slurry to flow out was measured, the efficiency of the reagent's action in per cent being determined by calculating the change in fluidity due to the additive, as compared to the fluidity using water alone, the moisture content of the slurry remaining the same. For marl slurry the normal moisture content was taken as 39%. The mineral and organic substances that had been tested for grinding were also used as the diluent reagents.

The data secured in these experiments are reproduced in Figs 2, 3, and 4. As Fig. 2 indicates, caustic soda, soda, and (to a lesser extent) water glass at first liquefy the slurry appreciably, increasing its fluidity at low concentrations, in the case of a marl slurry in distilled water. As the reagent concentration is raised, little further change in liquefaction occurs, the curve passing through a flat, prolonged maximum and then dropping off, the slurry turning into a pasty mass.

The interval of maximum liquefaction is greater for soda than for caustic soda.

It should be noted that in the region of high concentrations, starting at

0.1%, any further addition of small quantities of a concentrated solution of caustic soda or of water glass results in the formation of minute flakes or lumps, the whole slurry thickening. These lumps break down, however, after stirring and standing for 5 to 15 minutes, the slurry reacquiring its original fluidity. In view of this, we determined the fluidity after allowing at least 5 minutes to elapse after the reagent had been added. We have found that the slurry does not thicken after prolonged standing, but rather grows somewhat more liquid for all concentrations of alkaline electrolytes.

A peat extract in caustic soda produces appreciable liquefaction of the slurry even at minute concentrations (Fig. 2, Curve 5), this fluidity persisting at higher concentrations as well. The relative increase is about 30%. The same sort of extract is less active in water glass in this respect (Fig. 2, Curve 4). The effect of reagents upon the fluidity of a marl slurry prepared with tap water is likewise evident in Figs. 3 and 4. Syrup does not cause thickening; on the contrary, it slightly increases fluidity, even at low concentrations, after which the fluidity is practically unaffected (Fig. 3, Curve 2). Pure sulfite-cellulose lye is more effective in tap water than it is in distilled water, causing an approximately 100% increase in the fluidity of the slurry (Fig. 3, Curves 3 and 4). Here, too, a mixture of sulfite-cellulose lye and caustic soda produces a very considerable overall effect, greatly increasing the fluidity of the slurry (Fig. 4, Curve 1). Caustic soda exhibits the same variation of fluidity with concentration and the same liquefaction maximum in tap water as in distilled water. A mixture of peat extract and soda produces a considerable rise in fluidity, the subsequent addition of water glass causing some additional increase in fluidity.

Thus, a mixture of sulfite-cellulose lye and an alkali proved to be the most efficient additive in this instance as well, producing an increase of some 35% in fluidity.

The marl we used consisted, in the main, of 60% calcium carbonate and 40% argillaceous material. The various reagents were reacted with carbonates and argillaceous materials separately in order to ascertain the liquefying effect of the reagents upon the marl slurry; the materials used were Belgorod chalk and Glukovetsk kaolin.

Our results are plotted in Figs. 5 and 6. These graphs indicate that

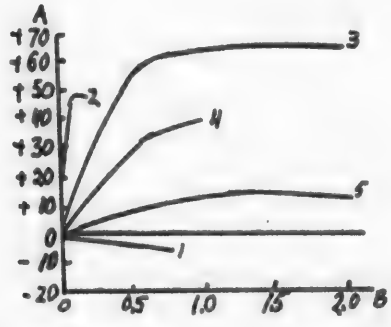


Fig. 5. Fluidity of chalk slurry as a function of reagent concentration.

A-% change of fluidity; B-% reagent (by weight of solid).

1-NaOH; 2-peat extract in waterglass; 3-sulfite-cellulose lye; 4-syrup; 5-sugar.

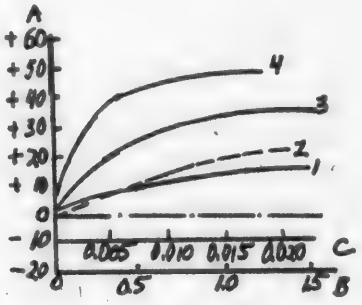


Fig. 6. Fluidity of kaolin slurry as a function of reagent concentration.

A-% change of fluidity; B-concentration of syrup; C-concentration of Na_2O and peat extract.

1-Syrup; 2-peat extract with $Na_2O \cdot n\ SiO_2$; 3-sulfite-cellulose lye; 4-sulfite-cellulose lye in an alkaline medium pH = 8.3.

caustic soda has no effect upon a chalk slurry at any concentration up to 1% (Fig. 5, Curve 1). A peat extract produces a very strong liquefying effect, increasing the fluidity by some 45% (Fig. 5, Curve 2). Sugar and syrup increase the fluidity; this is particularly true of syrup, whose efficiency is about 40% in this respect (Fig. 5, Curves 4 and 5). Sulfite lye proved to be an extremely powerful liquefier of chalk slurry, its efficiency totaling some 70% and actually not depending upon the presence of caustic soda at all (Fig. 5, Curve 3). The effect of alkalies and of alkaline salts upon the fluidity of kaolin (slip) is well-known: at low concentrations they usually act as liquefiers, while at higher concentrations they cause thickening. According to other researchers [5], peat extract is a very good peptizer and stabilizer of kaolin suspensions. Using this extract with kaolin slurry yielded good results; about the same effect was obtained with the addition of syrup, as may be seen in Fig. 6 (Curves 1 and 2). The same graph indicates that here, again, the most powerful diluent is sulfite lye in an alkaline medium (Curves 3 and 4), its liquefying efficiency being 40 to 50%, or much higher than the peat extract value.

We may conclude from these data that the liquefaction of marl slurry by alkaline reagents is apparently governed by the behavior of the argillaceous material, inasmuch as they do not affect chalk. The strong liquefying action of peat extract and of sulfite-cellulose lye in an alkaline medium upon marl slurry is due to their action upon both of the constituents of the marl. Thus, the reagents and reagent mixtures that strongly liquefy carbonate and argillaceous materials in similar concentrations prove to be the most effective liquefying agents for marl slurry as well.

Effect of reagents upon the fluidity of the slurry of the Amvrosievsk cement plant.* We endeavored to establish the possibility of lowering the moisture content of the Amvrosievsk cement plant slurry by adding diluents; the slurry and the water were received from the plant in May, 1948. The chemical analysis of the slurry and the water is given below.

Screen residues of the slurry: 0.6% on a screen with 900 openings per cm^2; 3% on a screen with 4900 openings per cm^2; and 4.2% on a screen with 10,000 openings per cm^2.

The best reagents and mixtures were used as liquefying additives, the optimum concentrations being established all over again. The fluidity was measured gravimetrically in the instrument mentioned above, i.e., we measured the weight of slurry flowing out of the device per unit time. The effect of various additives at various concentrations was estimated by comparing the weights of slurry of identical moisture content that flowed out of the device in 9 seconds; it was expressed in per cent. For example, 50 g of slurry with a moisture content of 50% but without any additive flowed out during this interval of time, while 75 g of slurry containing 0.04% caustic soda (in terms of Na_2O) by weight of the dry slurry as an additive flowed out. Hence the comparative increase in fluidity was $\frac{75 - 50}{50} \cdot 100 = 50\%$.

Chemical Analysis of Slurry, %

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Calcining losses	Total	Titer	Moisture
14.88	1.33	2.68	44.26	0.71	36.48	100.34	77.98	51.33

Chemical Analysis of Water (Mg per Liter)

SiO_2	R_2O_3	CaO	MgO	SO_3	Cl	Calcining losses	Solid residue	Matter in suspension at 105°C
69.2	2,0	135.96	68.38	309	244.4	169.0	901.0	43.8

*Engineer I. Ya. Piven and Analyst N. G. Smilyanskaya participated in this portion of the work.

The comparative liquefying action of some additives upon the slurry of the Amvrosievsk cement plant is given in Table 4.

TABLE 4

Liquefying Effect of Various Additives Upon the Slurry of the Amvrosievsk Cement Plant

Additive	Concentration of additive, % by weight of dry slurry *	Relative increase in fluidity, per cent
Caustic soda	0.04	50
Soda	0.04	20
Water glass	0.04	50
Sulfite lye	0.15	70
Syrup	0.70	11
Peat extract in water glass	0.04	70
Mixture of sulfite lye and soda	0.15 and 0.04	120
Peat extract in soda	0.08	70
Mixture of sulfite lye and caustic soda.	0.15 and 0.04	132
Ammonia	0.04	(-40), resulting in thickening
Mixture of sulfite lye and water glass..	0.15 and 0.04	75

As Table 4 indicates, the strongest diluents were the combined additives, consisting of an organic substance (sulfite-cellulose lye or humous substances) and an alkaline electrolyte (sodium hydroxide or soda). The liquefying effect of such combined mineral and organic substances rose appreciably even at relatively low concentrations of each of the diluent's constituents. As for the effect of the reagent concentration upon the fluidity of the slurry, the patterns of behavior were the same as those observed in the laboratory for the marl slurry, viz.: as the concentration of alkalies or alkaline salts in the slurry rises, liquefaction increases at first, reaching a maximum value at a certain concentration. As more electrolyte is added, the fluidity of the slurry begins to decrease noticeably, until the slurry finally solidifies entirely; organic additives increase fluidity sharply, from the very start, as their concentration is raised, but after a certain level has been reached, further increases in the additive concentration produce no essential change. When mixtures of electrolytes and organic substances are used, the liquefying effect rises rapidly, reaching high values at extremely low percentages of alkali. Increasing the concentration of the latter intensifies liquefaction, the concentration range in which liquefaction is a maximum spreading out, which eliminates the danger of an excess of the electrolyte causing the slurry to solidify.

It should be added that the fluidity increases somewhat with time when the liquefied slurry is allowed to stand.

EVALUATION OF RESULTS

We determined the extent of the stabilizing action of the additives as a function of their concentrations in order to ascertain the mechanism of their action in the dispersing of marl and in liquefying marl and chalk slurries. We did this by determining the amount of volumetric shrinkage, the settling rate of the suspension, and the value of the zeta-potential. Most typical was the variation of the zeta-potential with the concentration of the reagent (soda). During these determinations the stability of the marl suspension was visually observed to

* Concentration of alkali given in terms of Na_2O.

change parallel with the change in the zeta-potential. When soda was added to the marl suspensions, the pH and the zeta-potential both changed considerably, the latter rising, passing through a maximum, and then falling as the soda concentration was raised.

No charge was found on the particles in a suspension of Belgorod chalk to which soda had been added.

The addition of sulfite-cellulose lye alone to chalk and marl suspensions yielded a neutral or alkaline reaction (the solution of sulfite-cellulose lye was acid), practically no zeta-potential being observed; at the same time the sulfite-cellulose lye exerted an extremely powerful liquefying effect upon the marl and chalk suspensions, as has been noted above.

According to Rebinder, stabilizers (peptizers) of a suspension are, as a rule, also hardness reducers during wet dispersing [4]; he considers the peptization process to be a dispersing of the aggregates with the application of the minimum mechanical effort (stirring).

The formation of adsorbed ionic and molecular layers on the particles of the material being pulverized increases the affinity of the liquid for the solid and reinforces the loosening action of the thin layers of liquid that penetrate into the microfissures, decreasing the strength of the material and facilitating its disintegration. The formation of adsorption layers likewise affects the internal friction of the suspension and its fluidity.

According to our experiments, marl manifests a direct relationship between the stabilizing action of the reagent and its liquefying effect – the stronger stabilizers are also the better liquefiers, the weaker stabilizers or coagulators have little effect upon the liquidity of the slurry or else diminish it.

The accelerating effect of additives upon the rate of grinding conforms to their liquefying and stabilizing action: stabilizers speed up grinding, while coagulators slow it down. Acids (hydrochloric and carbonic) constitute somewhat of an exception to this rule; though they are weak coagulators of a marl suspension, they accelerated the rate of grinding. Here we have chemical reaction between the reagent and the raw material, in addition to the adsorption effect, which results in breaking down the latter's structure.

The data cited on the positive effect of alkaline reagents upon the liquefaction of slurries is in complete agreement with the results of other authors [2,3], though we have demonstrated the linear relationship between the degree of liquefaction, stabilization, zeta-potential, and acceleration of dispersion when alkaline electrolytes are added.

As for the effect of other reagents, namely, the organic ones, strong stabilizers, such as peat extract with alkalies and sulfite-cellulose lye in an alkaline medium, also act as good liquefiers.

The effect of syrup upon fluidity is apparently related to its reaction with the cations of coagulators, since syrup even diminishes the fluidity of marl slurry in distilled water, though it increases fluidity somewhat in tap water when used in the same concentration (Fig. 3, Curves 1 and 2); the effect of syrup on the fluidity of kaolin slurry is negligible, though somewhat greater on chalk slurry (Fig. 6, Curve 1, and Fig. 5, Curve 4).

Separate experiments on chalk and kaolin slurries showed that the best liquefiers of marl slurry happen to be those that also liquefy chalk and argillaceous slurries.

The weak liquefying action of caustic soda on marl slurry is due to the fact that it does not stabilize or liquefy the calcium-carbonate component –

chalk (Fig. 5, Curve 1), so that the use of caustic soda alone as a liquefier, as is sometimes recommended, is not advisable. Even less advisable is the use of soda alone, compared to such powerful liquefiers as a mixture of peat extract and soda or sulfite-cellulose lye in an alkaline medium.

Other authors have previously pointed out the positive action of sulfite-cellulose lye and caustic soda, each by itself, in increasing the fluidity of slurries, but – as our experiments have shown (and as is seen most clearly in Fig. 4) – the combined use of these reagents results in a very considerable liquefying effect even at extremely low concentrations of the alkaline electrolyte. Moreover, maximum liquefaction occurs at comparatively low reagent concentrations, which is important in the industrial application of such a combined liquefier (peptizer). When we recompute our data on the relative increase in fluidity due to the introduction of additives, making the necessary interpolations, we find that peat extract and sulfite-cellulose lye with soda reduce the moisture content of the slurry by 5-7% by weight of the marl slurry, and by some 10% by weight of the chalk slurry, or by 10-15% and 20%, respectively, of the weight of the water added. The attainable reduction in the moisture content of the slurry of the Amvrosievsk cement plant without impairing its fluidity is 6% by weight of the slurry or 12% by weight of the water when peat extract is used in water glass, for 1.2 kg of Na_2O per ton of dry slurry and a consumption of 0.5 kg of lignite (containing 45% humic acid) per ton of dry slurry. When the Na_2O content is higher – 3.3 kg – and the consumption of lignite is 1.5 kg per ton of dry slurry, the attainable reduction is 8% by weight of the slurry and 16% by weight of the water.

When 1.5 kg of sulfite-cellulose lye and 0.5 kg of soda or 0.25 kg of caustic soda to 1.0 kg of water glass are added per ton of the dry slurry, we can reduce the moisture content by 6% of the slurry by weight (or 12% of the water by weight). The same effect may be attained with the use of lignite or peat extracts in soda, using 2.0 kg of Na_2O and 0.5 kg of lignite per ton of dry slurry.

The reduction in the moisture content may be increased to 7-10% by increasing the percentage of alkaline electrolytes somewhat, so that we can obtain the same fluidity for a (Amvrosievsk) slurry moisture content of 42-45% as we otherwise get for a moisture content of 51.3%.

Preliminary calculations indicate that reducing the moisture content of slurry by 6% would increase the productivity of rotary kilns by 7%, while reducing the fuel consumption per output unit by 7%.

SUMMARY

Use of the combined additives suggested by the authors as liquefiers – dispersion accelerators – should also increase the capacity of the equipment used for the pulverizing and agitating (liquefying) of the raw materials, improve the technical properties of the slurry, and above all, make possible a considerable reduction in the slurry's moisture content.

Besides increasing the productivity of the apparatus used to grind and liquefy the materials, the introduction of the recommended liquefiers also makes it possible to increase the output of rotary kilns and to reduce the unit fuel consumption required for calcining.

LITERATURE CITED

[1] P.P.Budnikov, G.B.Kukolev, and V.M.Lezhoev, Trans. Central Laboratory Ukraine Refractory and Cement Trust, Kharkov (1932).

[2] P.D.Kevesh, A Study of the Effect of Adding Caustic Soda Upon the Fluidity of Slurry. Coll. Research Papers All-Union Cement Research Institute, 16 (1937).

[3] V.V.Tovarov, Cement, 11-12 (1946).

[4] P.A.Rebinder, L.A.Shrainer, and I.F.Zhigach. Reducing Hardness During Drilling, USSR Acad. Sci. Press, Moscow-Leningrad (1944).

[5] G.V.Kukolev and I.Ya.Piven, Trans. C.M.Kirov Institute of Chemical Technology, Kharkov, 6, (1947).

Received February 12, 1950.

NONWIRE PORCELAIN RESISTORS WITH A CARBON LAYER

A. I. Miklashevsky and P. I. Uspenskaya

Not many papers have been published on nonwire resistors, and there is practically no material available on the composition of the porcelain used for nonwire resistors, on the methods of preparing these resistors, or on the physicochemical principles underlying their manufacture.

A paper by Carter, in which high-ohmage resistors with a carbon coating are described, is of some interest. The paper gives no indication, however, of the composition of the ceramic bases used or of their properties.

Some references in the literature tell us that the bases for high-ohmage resistors are sand-blasted, while etching of the surface with hydrofluoric acid is used for low-ohmage resistors.

The Journal of Technical Physics has published a paper by V.T.Renne and Kh. Kh.Renne [1], in which the authors point out that the resistance rating depends upon the temperature of carbonization at constant pressure. The authors assert that this type of resistor consists of a carbon-ceramic layer.

A paper by Planer states that the carbon in nonwire resistors is a crystalline solid and that its conductivity differs from that of ordinary graphite. The major advantage of resistors of this type is their low temperature coefficient, 0.02-0.07% per °C. A pyrolitic carbon resistor, in which the temperature coefficient is compensated by the expansion of the porcelain base, may be prepared by suitably choosing the material used for the base. The author also points out that the resistor's temperature coefficient rises for thinner layers of carbon.

Ranger's review gives a schematic summary of the carbonization of ceramic bars and tubes in vacuum electric furnaces. The thickness of the carbon layer is about 0.001 mm for some resistors, its temperature coefficient being $3 \cdot 10^{-4}$ per °C.

Before the war porcelain for nonwire resistors was manufactured in the shape of cylindrical tubes by the Lomonosov factory, the First of May factory, and others, but this manufacture was of a casual nature, and only during the past few years has systematic research been undertaken, as a result of the growing use of nonwire resistances.

It was the objective of the research project described in the present paper to find general principles governing the selection of ceramic ware for porcelain resistor bases, to explore the nature of the carbon layer, and to establish the optimum conditions for bonding of the carbon to the ceramic ware. In our investigations we employed resistors manufactured by the State Institute of Ceramic Research and Design (GIKI), which were compared with foreign specimens (standard samples).

EXPERIMENTAL

Small tubes of high-voltage porcelain, of various lengths and diameters,

some of them having sand-blasted surfaces, were used as the bases for our nonwire resistances.

Chemical analysis of the standard samples yielded the following results in per cent:

SiO_2 68.46, TiO_2 0.34, Al_2O_3 24.90, Fe_2O_3 0.78, CaO 0.35, MgO 0.21, K_2O 5.06, Na_2O 0.60.

Mineralogical analysis indicated that the particles of quartz in the porcelain bases were fused, the fusion zone being 1 μ, that the feldspar and the basic mass were largely mullitized, that the pores were sealed and rounded, 10-15 μ in size, though sometimes being as large as 20 μ.

The refractoriness of the porcelain ware, as determined in a Kryptol furnace, lay in the 1650-1700° range.

This comparatively high refractoriness compelled us to make qualitative tests for the presence of beryllium and zirconium oxides in the material; it was found, however, that the porcelain contained practically no beryllium or zirconium oxide.

The physical characteristics of the porcelain ware were as follows:

True porosity	6.60-6.92%,
Sealed porosity	6.56-6.87%,
Apparent porosity	0.04-0.05%,
Density	2.44-2.46 g/cm^3,
Weight per unit volume	2.28-2.29 g/cm^3,
Ultimate bending strength ...	973.5-1040 kg/cm^2

As these figures indicate, the mechanical strength of the porcelain is rather high, and the body is fully sintered.

Chemical analysis of the carbon layer, by the Lucy and Brody test, led us to conclude that we were dealing with a graphite layer. (The samples carbonized in the GIKI exhibited the same behavior).

In view of the extraordinary thinness of the carbon layer, of the order of thousandths of a millimeter, and hence its negligible weight, it was found to be impossible to make an X-ray analysis of this surface layer. When we peeled or scraped off this layer, the material we secured was contaminated. We therefore prepared nonwire resistors with a thicker carbon coating by depositing a carbon layer on the porcelain ware by cracking gasoline at a higher temperature, 950-1050° C in an atmosphere of nitrogen (this cracking is ordinarily done at 900-950°C).

The carbon layer deposited upon the porcelain ware at a higher temperature adhered less firmly, but we still got a highly contaminated material when we removed it by mechanical scraping.

After several trials, we decided to employ the so-called "thermal shock" method, i.e., plunging the incandescent resistors into cold water as soon as the carbon had been deposited. This caused the carbon layer to spall from the surface of the porcelain ware into the water in thin petals; filtering the latter gave us our required carbon. This method is not suitable for every porcelain, as will be seen below. But this experiment shed light on several factors governing a search for a qualitative method of determining the strength with which the carbon layer was attached to the porcelain.

The carbon layer thus collected was practically free of foreign impurities and could be used in X-ray analysis. This was performed* with an X-ray tube possessing an iron target, using the Debye-Scherer method, using a flat film, with

*This reserach was done in the Physical Institute of Leningrad State University.

the following operating conditions: V_a = 50 kv, anode current I_a = 12 mA.

The photograph (Fig. 1; See Plate, page 277) shows 3 diffraction rings against a background of a Laue crystallogram of mica (the sample was applied as a paste in a layer 1-1.2 mm thick to a mica backing). The diffraction rings are caused by the sample.

Calculations and comparison of our data with those in the tables indicated that the sample consisted of graphite, the interplanar distances of which, as taken from the tables, agree with the corresponding values obtained in the present research within the limits of experimental error, (about 1%), as may be seen from Table 1.

The specific gravity of this material was 2.26; this also indicated that the material was graphite (the mean specific gravity of graphite is 2.25). Determination of the carbon content indicated that the material contained over 95-96% carbon.

TABLE 1

Results of X-Ray Analysis of the Structure of the Samples

Ring	Ring radius, cm	sin f	Interplanar distance d, Å		Δ d
			Experimental	From Tables	
1	1.55	0.229	3.79	3.80	0.04
2	1.70	0.248	3.48	3.45	0.04
3	1.93	0.274	3.17	3.13	0.04

Efforts to measure the thickness of the carbon layer microscopically (say, in an end view of the cylinder) were unsuccessful. In many samples the ring of graphitic material did not have a sharp edge, but gradually grew thinner, merging into the porcelain ware. We therefore computed the thickness of the graphite layer as follows: 20 identical porcelain bases from a single batch were placed in a heated tubular Mars furnace in an oxygen atmosphere. The amount of carbon dioxide absorbed by ascarite was determined by weighing on an analytical balance, converted into carbon, and referred to a single bar. Then, the thickness of the carbon film was calculated from the surface of the developed cylinder and the specific gravity of the material.

Two batches of porcelain ware were carbonized. The carbonizing times differed, though all the other conditions remained the same. The test results are listed in Table 2.

TABLE 2

Determination of the Thickness of the Carbon Film Deposited on Porcelain Ware

Sample No.	Carbonizing time, min.	Number of resistors	Weight of CO_2 for 20 porcelain bases	Weight of carbon film on a single bar, $g \cdot 10^{-4}$	Film thickness, μ	Resistance, ohms
1	5	20	0.0018	0.25	0.03	6050
2	10	20	0.0051	0.70	0.10	3000

As we see from Table 2, the thickness of the film is between 0.03 and 0.1μ for resistances between 3000 and 6000 ohms;* increasing the carbonizing time increases the thickness of the film and lowers the resistance value. Subsequently the thickness of the films was measured on a much larger scale in many of our own samples of nonwire resistors; these measurements bore out the foregoing conclusions.

One of the objectives of the present research has been to establish the conditions governing a good bond between the graphite layer and the porcelain backing.

*The calculations were based on the assumption that the carbon layer is continuous in low-ohmage resistors.

The graphite was well bonded in the samples of porcelain tested, hardly spalling off at all during "thermal shock"; in some (experimental) porcelains the graphite was not firmly attached and came off easily during "thermal shock" treatment, though it was changed into a lacquer-smooth coating during operation of the resistors. We assumed that this phenomenon was due to the differences between the coefficients of linear expansion of various grades of porcelain. The coefficient of linear expansion of the porcelain should be as close as possible to that of graphite.*

We were unable to measure the c.l.e. of graphite in the present research, though we did measure the c.l.e of various porcelains at various temperatures, ranging from 150 to 1150°C, by means of a high-temperature dilatometer.

When we compare the coefficient of linear expansion of Acheson synthetic graphite and of natural graphite with that of the porcelain in a standard resistor, we see (Figs. 2 and 3) that the c.l.e. of the porcelain is close to that of the Acheson synthetic graphite. It was assumed that the thermal behavior of the porcelain must be the same as that of the graphite; the better this agreement, the more firmly will the graphite be bonded to the porcelain. The nature of the

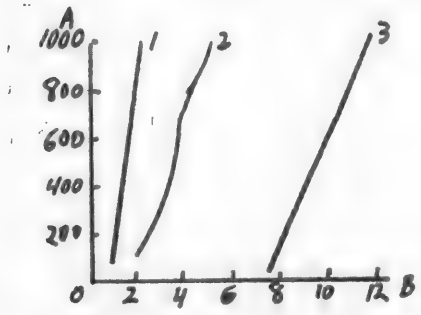


Fig. 2. Coefficient of linear expansion of porcelain and graphite as a function of temperature.

A-Temperature, °C; B-coefficient of linear expansion, °C x 10^{-6}.

1-Acheson graphite; 2-standard porcelain; 3-Botogolsk graphite.

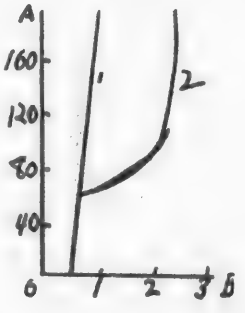


Fig. 3. Coefficients of linear expansion of porcelain and graphite at low temperatures.

A-Temperature, °C; B-coefficient of linear expanison, °C x 10^{-6}.

1-Acheson graphite; 2-standard porcelain.

surface of the porcelain is likewise an essential factor. Figure 3 shows that at temperatures up to 100°C (a possible operating temperature for nonwire resistors), the c.l.e. of porcelain is still closer to that of graphite, actually intersecting the graphite curve at 60°C.

On the basis of this study of the resistors, we prepared a number of experimental porcelain pastes, of differing compositions and properties (Tables 3, 4, 5, and 6).

We bore in mind that the proportion of feldspar determines the glassy state of the porcelain, affects crystallization, and, as it contains potassium and sodium oxides, which have a high coefficient of expansion, greatly affects the behavior of the paste as a whole.

The porcelain ware made from the test pastes were subjected to physical tests: determination of their refractoriness, coefficient of linear expansion, etc.

The proportions of Paste No. 3 were worked out in 1946 by the GIKI. Tables

---

*Hencef rth we shall use the abbreviation c.l.e. for the coefficient of linear expansion.

TABLE 3

Constituents of Porcelain Test Pastes, in Per Cent

Material	Paste No.							
	1	2	3	4	6	7	8	9
	Firing Temperature							
	1320	1320	1280	1220	1160	1350	1350	1280
Feldspar	3.0	25.0	36.0	49.0	68.0	11.0	10.0	35.0
Prosyanovsk kaolin	45.0	35.0	30.0	24.0	15.0	23.0	68.0	26.0
Chasovyar clay	32.0	15.0	14.0	11.0	7.0	26.0	22.0	20.0
Quartz sand	–	25.0	15.0	12.0	7.5	40.0	–	19.0
Porcelain crock	20.0	–	5.0	4.0	2.5	–	–	–
Total	100	100	100	100	100	100	100	100

TABLE 4

Computed Chemical Composition of Porcelain Test Pastes, Per Cent

Constituent	Paste No.								Standard porcelain
	1	2	3	4	6	7	8	9	
SiO_2	58.58	69.43	68.99	66.50	66.30	78.85	55.65	67.95	63.46
TiO_2	0.99	0.51	0.50	0.38	0.22	0.34	0.30	0.26	0.34
Al_2O_3	36.20	24.50	24.16	24.20	22.24	20.28	39.70	24.78	24.90
Fe_2O_3	0.86	0.51	0.53	0.44	0.32	0.34	0.45	0.33	0.78
CaO	0.78	0.58	0.73	0.80	0.98	0.58	1.00	0.79	0.35
MgO	0.44	0.26	0.22	0.21	0.15	0.28	0.50	0.28	0.21
K_2O	1.60	3.22	3.50	5.71	7.50	1.96	2.04	4.46	5.06
Na_2O	0.65	0.99	1.37	1.76	2.29	0.37	0.36	1.15	0.60
Total...	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 5

Refractoriness of Porcelain Test Pastes

Paste No.								Standard porcelain
1	2	3	4	6	7	8	9	
1600°	1550°	1580°	1480°	1360°	1670°	1370°	1660°	1700°

3 and 4 show that Paste No. 9 resembles Paste No. 3 in its constituents and chemical composition. Its refractoriness is much different, however (Table 5), being close to that of the standard porcelain.

The physical characteristics of the test pastes indicate that Pastes Nos. 1 and 3 are the best sintering ones, while Pastes Nos. 9 and 4 have the highest mechanical strength.

Determination of the coefficients of linear expansion indicated that the bonding strength of the carbon was higher for the porcelain whose c.l.e was closest to that of the standard (Fig. 4), inasmuch as the carbon did not spall from such porcelain even under "thermal shock". The graph shows that the pastes with the most feldspar (Nos. 4 and 6) are farther from the test porcelain and the

expansion curve for graphite. The c.l.e. of the Pastes Nos. 1, 7, and 8 are closest to that of the test paste, but their chemical compositions are not the same; they have the least feldspar and contain less alkali; moreover, their percentages of other constituents (SiO_2, Al_2O_3) also differ.

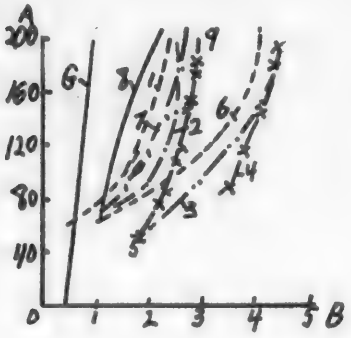


Fig. 4. Coefficients of linear expansion of various porcelain pastes.

A-Temperature, °C; B-c.l.e. G-graphite.

1-Paste No. 1; 2-standard sample; 3-paste No. 3; 4-paste No. 4; 6-paste No. 6; 7-paste No. 5; 8-paste No. 8; 9-paste No. 9.

The "thermal shock" test results agree with the expansion curves for all the test pastes.

Our results indicate that Paste No. 3, and especially Paste No. 9, are closer to the desired paste in several respects.

Our mineralogical analysis indicated that Pastes Nos. 7 and 9 are the most highly mullitized; we know that mullite has a low coefficient of linear expansion, so that its presence in our porcelain is highly desirable. Owing to its refractoriness and mullitization, Paste No. 9 could be fired at a higher temperature (above 1280° C), which would yield a still higher degree of mullitization.

Taking the Paste No. 9 worked up by us as the optimum, we now cite the results of comparative tests of the electrical properties of the standard nonwire resistors and the resistors manufactured with Paste No. 9. The conditions under which the hydrocarbon (gasoline) was cracked were the same in both cases, (Table 7).

TABLE 6

Physical Characteristics of Porcelain Ware Made from Test Pastes

Characteristic	Paste No.							
	1	2	3	4	6	7	8	9
True porosity, %	7.70	7.60	9.10	5.50	9.80	10.30	9.00	10.70
Sealed porosity, %	7.63	7.41	9.05	5.0	9.38	9.91	8.68	10.54
Apparent porosity, %...	0.07	0.19	0.05	0.07	0.42	0.39	0.32	0.16
Density, g/cm^3	2.42	2.42	2.47	2.45	2.42	2.51	2.58	2.51
Wt. by volume, g/cm^3 ..	2.23	2.24	2.25	2.32	2.18	2.14	2.37	2.18
Bending strength, kg/cm^2	923.7	866.8	826.2	1084.7	743.8	823.5	951.2	973

The test results indicate that Paste No. 9 is close to the standard in its electrical properties, even surpassing it in some respects.

The porcelain ware was covered with graphite in a nitrogen atmosphere in a tubular furnace at 900-950°C. The nitrogen, at a definite pressure, passed through a bottle full of gasoline and carried vapor of the latter with it, this gaseous mixture entering the tubular furnace, heated to 900-950°, which was filled with the porcelain ware (Fig. 5; see Plate, page 277). Purifying apparatus is cut in along the line.

The optimum pyrolysis temperature was found experimentally to lie between 900 and 1000° (Table 8).

When we considered the resistance of graphitic layers and their thickness, we assumed that the magnitude of very high-ohmage coatings (of the order of 1 megohm) and of low-ohmage coatings (of the order of 200 ohms) will not be linear

TABLE 7

Electrical Stability Characteristics of Resistors Made of Porcelain Ware

Name of sample	Nameplate rating, watts	Resistance, ohms	Temp.* coefficient, °C	Aging factor** after running resistor 100 hrs. at 150% of nameplate rating, %	Temperature stability factor *** (cyclic), %	Humidifying factor**** (boiling for 20 minutes), %
Standard porcelain....	0.5	10750	$1.8 \cdot 10^{-4}$	2.2	0.45	0.6
Porcelains from Paste No. 9.....	0.5	9130	$2.1 \cdot 10^{-4}$	1.9	0.10	0.7

functions of the thickness of the graphitic layer. Otherwise, we should have to assume the existance of coatings with a thickness of thouandths of a micron, which is unrealistic. Apparently, in relatively thick layers, the graphitic coating must behave differently than in very thin layers.

In the thin layers of high-ohmage resistors (i.e., containing a small quantity of graphite), the graphite coating is a resistor consisting, possibly, of individual spots that conduct current, and in view of the highly insulating properties of the porcelain base, the passage of the current is discontinuous, so to speak.

We applied graphite layers of various thickness, and hence of various resistance (for identical rod dimensions) by varying the cracking conditions, in order to test this assumption on actual porcelain ware. We measured the electrical resistance and the graphite film thickness of these coatings by the method described above. The observed variation of the resistance with the thickness of the graphite film is summarized in the curve of Fig. 6, which shows that the resistance of the samples rises but slightly as the thickness of the graphite film is diminished from 1 to 0.2-0.1 μ, though the resistance of the samples rises sharply when the thickness of the film is reduced below 0.1 μ. This observation testifies to the feasibility of preparing resistors with extremely high ohmage by reducing this conventional "thickness" of the graphite film to no more than

---

* According to official technical specifications, the temperature coefficient should not exceed $6 \cdot 10^{-4}$ per °C for resistors with ratings up to 1,000,000 ohms throughout the temperature interval from +20 to +70 °C.

** The aging factor should not exceed +4% after load.

*** The mean value of the temperature stability factor (for the given type and size of resistors) should not exceed 1% after two cycles of varying the temperature from +85 to -60 °C. The ohmic resistance of the samples under normal conditions, R_1, is measured, after which the samples are subjected to cyclic heating to +85 ° and chilling to -60 °C at standard relative humidity. After this cycle has been repeated, the resistance is measured again, R_2, and the factor is computed from the formula:

$$K_C = \frac{R_2 - R_1}{R_1} \cdot 100\%.$$

**** The humidifying factor should not exceed +6% for resistors with ratings up to 1,000,000 ohms after the resistors have been kept in a chamber with a relative humidity of 95-98% at a temperature of 40 °C.

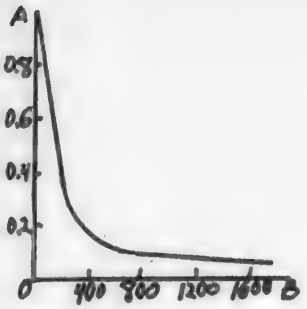


Fig. 6. Resistance of graphite as a function of the thickness of the film.

A-Increase in film thickness, microns; B-rise in graphite resistance, ohms.

TABLE 8

Cracking Conditions				
Test No.	Pressure, cm water column	Cracking time, minutes	Pyrolysis temperature, °C	Test results
99	2	10	800	No graphite deposited at all, no layer being visible.
101	2	10	900	Barely visible graphite layer.
102	2	10	1000	Graphite layer satisfactorily deposited.
103	2	10	1100	Good graphite layer, but not firmly bonded to porcelain; spalling off.

tenths and hundredths of a micron. This is an interesting generalization, but it requires further investigation, which goes beyond the scope of the present paper.

Study of several physical and chemical factors has shown that the standard porcelain is not the best backing for nonwire resistors of the carbon-ceramic type. Other pastes, such as Nos. 7 and 8, which contain small quantities of feldspar and more silica and alumina, might be better. For example, the coefficient of linear expansion of porcelain (one of the principal factors) is doubtless better in the Pastes Nos. 7 and 8 than in the standard paste; when we compare the samples with respect to their "thermal shock" behavior, we again find Pastes Nos. 7 and 8 superior; but the technology of their manufacture is more complicated (high firing temperature). The standard porcelain was a tried and tested backing for resistors of rather high quality; of the porcelain pastes we tried out Paste No. 9 had many properties that were closer to those of the standard than any of the others, in some respects even surpassing it. It has therefore been recommended for adoption in manufacture.

SUMMARY

1. The chemical composition of the porcelain studied is fairly constant: SiO_2 67-69%, Al_2O_3 24-26%, K_2O 4-6%, and is typical of a high-voltage porcelain. Its refractoriness ranged from 1650 to 1700°C. Its specific gravity was 2.440-2.460. Its weight by volume was 2.29. Its true porosity was 6.6-6.9%, its apparent porosity being 0.04-0.05%. Its bending strength was 1000 kg/cm^2, measured with an Ivanov-Stark machine.

2. The conducting layer is graphite, containing 95-96% carbon and with a specific gravity of 2.26, as shown by qualitative chemical tests, X-ray analysis, and specific-gravity measurements.

3. The thickness of the layer may vary from 0.03 to 0.1 μ for resistors of the order of 6000-3000 ohms.

4. The closer the coefficient of linear expansion of the porcelain is to that of the conducting carbon layer, the better will be the bond between the two.

5. A paste with the following composition: 35.0% Karelian feldspar; 26% Prosyanovsk kaolin; 20% Chasovyar clay; and 19% quartz sand has been recommended for the manufacture of nonwire resistors.

6. The optimum temperature for the hydrocarbon cracking process used to produce a coating on the porcelain is 900-1000°C.

7. The resistance is a complex function of the thickness of the graphite film; at thickness $< 0.1\ \mu$ the resistance will rise many times faster than the thickness of the film will decrease. This is evidence of the special nature of the arrangement of the carbon layer, which apparently conducts current discontinuously. Otherwise, we should have to assume that for high-ohmage resistors the thickness of the films drops to thousandths of a micron, which is unrealistic.

8. The porcelain we examined is not a porcelain with the optimum qualities. Some of the pastes prepared by us have demonstrated the feasibility of using other and superior compositions for nonwire resistors, such as alumina mullitized porcelains.

LITERATURE CITED

[1] V.T.Renne and Kh.Kh.Renne, J. Tech. Phys., 15, 9 (1945).

Received April 24, 1950

NONWIRE PORCELAIN RESISTORS WITH A CARBON LAYER

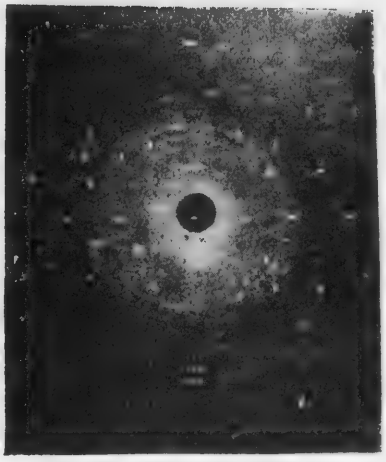


Fig. 1 X-ray photograph of graphite powder.

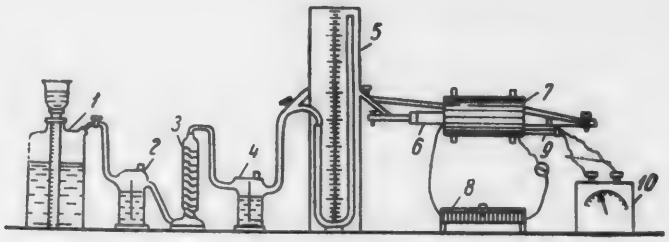


Fig. 5 Apparatus layout for Carbonization

1-Nitrogen tank; 2-Tischencko bottle containing pyrogallol; 3-Drexel bottle containing calcium chloride; 4-Tischencko bottle containing gasoline; 5-manometer; 6-porcelain tube; 7-tubular furnace; 8-Ruhstrat rheostat; 9-thermocouple; 10-galvanometer.

TREATING MANGANESE SLUDGES AND ORES WITH SULFUR DIOXIDE

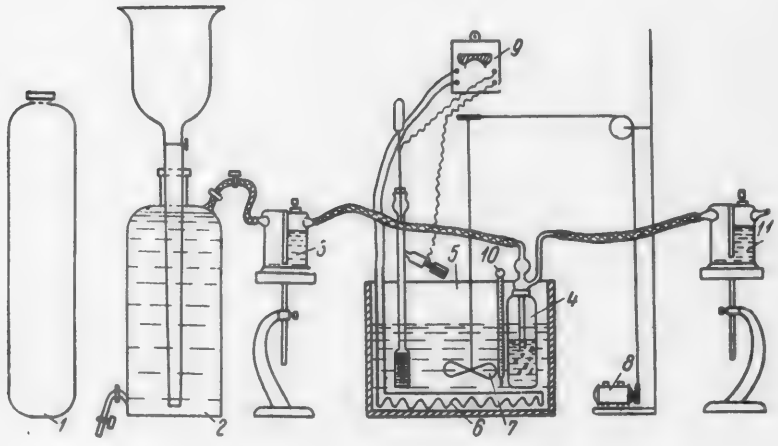


Fig. 1 Apparatus layout.

The notation is explained in the text.

TREATING MANGANESE SLUDGES AND ORES WITH SULFUR DIOXIDE*

V. M. Kakabadze

S. M. Kirov Polytechnic Institute of Georgia

Treating Manganese Sludges with Sulfur Dioxide

Of all the methods elaborated up to the present time, the method of extracting manganese from manganese sludges and ores by means of sulfur dioxide (sulfurous acid) merits the most attention. This process is based upon the reaction of manganese dioxide with sulfurous acid, giving rise to manganous sulfide and manganese dithionate [1].

Much research has been done on this abroad, and many patents have been taken out [2-23]. It has attracted particular attention in the USSR in connection with the maximum utilization of local raw materials and manufacturing wastes. Many research papers have also been published in this field here at home [24-38].

It must be said, however, that the research papers, proposals, and installations dealing with the sulfurous method are far from impeccable. In the present paper we have tried to bring some order out of chaos on several of the problems involved.

EXPERIMENTAL

Operational Procedure. The apparatus we employed is shown diagramatically in Fig. 1 (See Plate, page 277).

The sulfur dioxide was periodically drawn from the steel cylinder 1 into the graduated glass tank 2, where the gas was diluted with air to the required concentration. The diluted gas was passed through a Tishchenko bottle 3 filled with sulfuric acid to remove any impurities from the gas and to check on the steadiness of the gas supply. From 3 the gas passed to the Drexel reaction bottle 4, which contained the manganese suspension. The Drexel bottle was placed in a water thermostat 5, the water in which was heated by an electric heater 6. The water in the thermostat was kept in motion by the stirrer 7, driven by the motor 8. The temperature of the water was kept constant by means of a thermoregulator with the relay 9, the temperature being measured by the thermometer 10. The unreacted sulfur dioxide was passed through an absorber, a Tishchenko bottle 11 containing alkali, the residue being allowed to escape into the air. The Drexel bottle was rocked back and forth by a special device (not shown in the drawing). At the end of the run air was passed through the Drexel bottle to drive out the residual sulfur dioxide. The suspension was filtered into a 500-ml measuring flask. The precipitate was washed with water.

The amount of dissolved manganese and of the manganese combined as the dithionate was determined in the solution. The manganese was determined by the Volhard method, while the manganous dithionate was determined by the method used in the Institute of Chemistry of the Georgian Academy of Sciences [39]. The

difference between the total manganese and the manganous dithionate was the manganese in the form of the sulfate.

Preliminary tests. We first made tests with pure manganese dioxide.

When sulfur dioxide is reacted with manganese dioxide suspended in water, we get the dithionate:

$$MnO_2 + 2SO_2 \rightarrow MnS_2O_6. \qquad (1)$$

Part of the manganese dioxide is converted into manganous sulfate in accordance with the equation:

$$MnO_2 + SO_2 \rightarrow MnSO_4. \qquad (2)$$

The proportion of the dithionate to the sulfate depends upon the temperature. As the temperature is raised, the dithionate breaks down:

$$MnS_2O_6 \rightarrow MnSO_4 + SO_2, \qquad (3)$$

its percentage dropping.

Side reactions occur in the reaction apparatus, such as oxidation of the sulfur dioxide to sulfur trioxide by oxygen under the catalytic action of the manganese salts, resulting in the formation of sulfuric acid, etc.

Experiments have shown that no manganous dithionate is formed by the action of sulfur dioxide upon manganese sulfate, i.e., the reaction:

$$MnSO_4 + SO_2 \rightarrow MnS_2O_6 \qquad (4)$$

does not take place.

On the other hand, we found that the following reaction:

$$MnS_2O_6 + MnO_2 \rightarrow 2MnSO_4 \qquad (5)$$

takes place when manganese dioxide reacts with manganous dithionate in the presence of sulfur trioxide.

Tests made with no SO_2 present failed to produce this reaction. Hence, the SO_2 does not take part in this reaction directly, serving merely as an inductor.

The vigorousness of Reaction (5) is confirmed by thermochemical calculations.

Effect of various factors upon the extraction of manganese from manganese sludges. We used a pyrolusite sludge – Samples Nos. 17 and 18 – for these tests. We cite their percentage chemical composition (in terms of the absolutely dry substance).

Sample No. 17

SiO_2 – 29.50	MnO – 12.60	P_2O_5 – 0.59
Al_2O_3 – 2.20	CaO – 2.51	Moisture – 4.25
Fe_2O_3 – 5.49	MgO – 0.43	[Σ Mn – 37.58]
MnO_2 – 43.99	SO_3 – 0.54	

Sample No. 18

SiO_2 – 38.41	MnO – 2.59	SO_3 – 0.27
Al_2O_3 – 8.78	CaO – 2.55	P_2O_5 – 0.68
Fe_2O_3 – 3.32	MgO – 0.85	Moisture – 4.48
MnO_2 – 35.31	BaO – 2.51	[Σ Mn – 24.33]

10 g was used each time. Sludge No. 17 was used throughout, unless otherwise specified.

The effect of temperature upon this process is shown in Fig. 2.

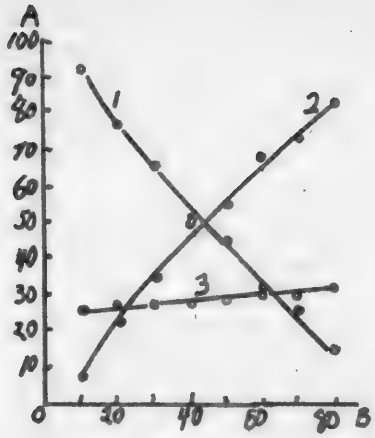


Fig. 2. Effect of temperature upon extraction of manganese from manganese sludges.

Experimental conditions: time-30 min.; fineness of grind - 200 openings per cm^2; SO_2 concentration - 13.05 - 13.65%; SO_2 quantity - 5 liters; solid: liquid ratio - 1:10. A-Mn entering solution, %; B-temperature °C; 1-MnS_2O_6; 2-$MnSO_4$; 3-ΣMn.

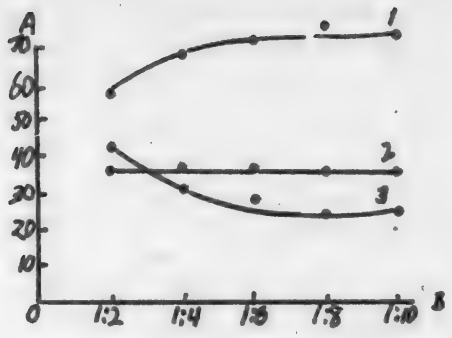


Fig. 3. Effect of ratio of solid-to liquid phases (solid:liquid) upon extraction of manganese from manganese sludges.

Experimental conditions: temperature - 80°; time - 30 min.; fineness of grind - 256 openings/cm^2; SO_2 concentration - 13.30%; SO_2 quantity - 5 liters

A-% Mn dissolved; B-ratio of solid: liquid pahses. 1-$MnSO_4$; 2-ΣMn; 3-MnS_2O_6.

As we see from Fig. 2, the extraction of manganese (ΣMn) increases as the temperature is raised from 10 to 80°. The dithionate predominates at lower temperatures, with the manganous sulfate predominating at the relatively high temperatures. In our experiments equal amounts of the manganous sulfate and dithionate were extracted at 45°.

The effect of fineness upon the process is shown in Table 1.

TABLE 1

Effect of Fineness of Grind Upon the Extraction of Manganese from Manganese Sludges

Experimental conditions: Temp. 60°; Time = 30 min.; Solid:Liquid Ratio = 1:10; SO_2 Concentration = 8.1-9.5%; SO_2 quantity = 5.0-5.82 liters.

No.	Fineness of grind, openings per cm^2	Dissolved manganese	
		Grams	Per cent
1	121	1.4815	39.42
2	256	1.4815	39.42
3	400	1.4815	39.42
4	900	1.4815	39.42

As the cited data indicate, fineness of grind has no effect upon the extraction of manganese. This is due to the fact that the sludge is a highly dispersed substance; in the dry state the caked mass forms lumps, but it returns to the initial dispersed state in water again. Thus the same criterion cannot be applied to sludges as to other substances, as far as fineness of grind is concerned.

The effect of the solid:liquid phase ratio (solid:liquid) is shown in Fig. 3.

The amount of manganese dissolved does not vary when the solid:liquid ratio is varied from 1:2 to 1:10. This must be due to the fact that the MnO_2 in the sludge readily reacts with the sulfur dioxide, so that within 30 minutes all the manganese that can be extracted by a given amount of sulfur dioxide enters solution no matter what its dilution. As dilution progresses, the percentage of manganous dithionate drops somewhat. On the other hand, we have found that the lower the solid:liquid ratio in the suspension, the less iron is dissolved, and

even more so the less phosphorus and other undesirable impurities. Hence, it is best to perform the extraction in moderately concentrated suspensions as far as diminishing the impurities in the solution is concerned; but it must be borne in mind that such suspensions are harder to handle (settling, filtration, etc.).

The results of our tests on the effect of SO_2 concentration are listed in Table 2.*

As we see in Table 2, raising the SO_2 concentration promotes the process; the reaction between the manganese and the SO_2 gains in intensity as the volume is decreased for equal quantities of SO_2. But this effect of the SO_2 concentration upon the extraction of manganese has its limits; a certain slowing down occurred in our experiments when the concentration reached approximately 25%.

The data on the effect of the quantity of SO_2 upon the extraction process are listed in Table 3.

TABLE 2

Effect of SO_2 Concentration Upon Extraction of Manganese from Manganese Sludges
Experimental conditions: Temp. = 80°; time = 30 min.; solid:liquid = 1:10; fineness of grind = 256 openings/cm^2

No.	SO_2 concentration, %	Quantity of SO_2, liters	Manganese dissolved	
			grams	per cent
1	2.53	13.8	0.7699	20.48
2	5.46	6.41	1.0278	27.34
3	10.54	3.32	1.2856	34.20
4	24.82	1.41	1.5576	41.44

To learn the effect of the quantity of SO_2 upon the formation of manganous dithionate we ran supplementary experiments, their results being listed in Table 4.

TABLE 3

Effect of the Quantity of SO_2 Upon the Extraction of Manganese from Manganese Sludges
Experimental conditions: Temp. = 80°; solid:liquid = 1:10; SO_2 concentration = 12.90-13.50%; fineness of grind = 256 openings/cm^2 ; rate of feed = 0.16-0.17 liters/minute.

No.	SO_2 quantity, liters	Mn/SO_2 ratio compared to the theoretical value	Time, minutes	Manganese dissolved	
				grams	per cent
1	4.37	1:0.4	25	1.4072	37.44
2	6.55	1:0.6	40	1.9413	51.39
3	8.68	1:0.8	55	2.0146	53.60
4	12.43	1:1 (theoretical)	75	2.6862	71.45
5	13.5	1:1.2	80	2.7884	74.20

TABLE 4

Effect of the Quantity of SO_2 Upon the Formation of Manganous Dithionate

Experimental conditions: Temp. = 80°; time = 30 minutes; solid:liquid = 1:10; SO_2 concentration = 14.98%; fineness of grind = 265 openings/cm^2

No.	SO_2 quantity, liters	Mn/SO_2 ratio compared to the theoretical value	Manganese dissolved, %		
			Σ Mn	Mn dithionate	Mn sulfate
1	4	1:04	55.89	17.84	82.16
2	10	1:1	68.92	18.20	81.80
3	12	1:1.2	70.42	20.28	79.72

*In this series of tests the concentration and volume of SO_2 were so chosen as to keep the quantity of SO_2 constant throughout all the tests.

As we see from these figures, increasing the amount of SO_2 passed through the suspension increases the amount of manganese extracted. Moreover, as the amount of SO_2 is increased, the amount of the manganous dithionate in the solution rises at the expense of a corresponding diminution of the percentage of manganous sulfate.

The effect of time on this process is shown in Table 5.

The results of auxiliary experiments run to ascertain the effect of time upon the formation of manganous dithionate are shown in Fig. 4.

TABLE 5

Effect of Time Upon the Extraction of Manganese From Manganese Sludges

Experimental conditions: Temp. = 80°; solid: liquid = 1:10; fineness of grind = 256 openings per cm^2; SO_2 concentration = 13.83%; quantity of SO_2 = 7 liters.

No.	Time, minutes	Manganese dissolved	
		grams	per cent
1	5	1.0989	29.24
2	10	1.4041	37.36
3	20	1.7491	46.54
4	30	1.7491	46.54
5	40	1.7643	46.94
6	60	1.7643	46.94

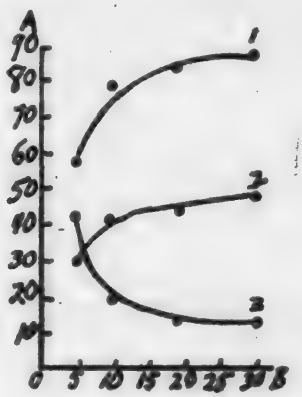


Fig. 4. Effect of time upon the formation of manganous dithionate.

Experimental conditions: Temp. - 80°; solid:liquid - 1:10; fineness of grind - 256 openings / cm^2; SO_2 concentration - 12.6%; quantity of SO_2 - 5 liters; A-Manganese dissolved,%; B-time, min.; 1-$MnSO_4$; 2-MnS_2O_6; 3-MnS_2O_6.

As this data indicates, time promotes the extraction of manganese, but only up to a certain limit (approximately 20 minutes). Thus, the reaction between pyrolusite sludge and sulfur dioxide is an intensive one, the extraction of the manganese being complete within a relatively short period of time.

The fact that the percentage of manganous dithionate decreases with time is worthy of note. This is apparently due to the fact that the manganous dithionate that is formed at first gradually disintegrates.

Investigation of the conditions governing the decomposition of the dithionate and the completeness of manganese extraction. We boiled the solution in order to effect the decomposition of the manganous dithionate, which is undesirable, since it causes losses and difficulties of a technological order. Samples were taken of the solution, prepared by the usual leaching, and the percentage of manganous dithionate it contained before and after boiling was determined. The Mn in the solution was taken as 100%.

The results of these tests are given in Table 6.

TABLE 6

Decomposition of Manganous Dithionate by Boiling the Solution

No.	Solution	Per cent in solution	
		Mn dithionate	Mn sulfate
1	Before boiling	60.80	39.20
2	After boiling: for 15 minutes	41.81	59.19
3	for 30 minutes	23.79	76.21
4	for 45 minutes	6.23	93.77

Thus, boiling the solution decomposes the manganous dithionate in accordance with Equation (3),

In addition, we determined the percentage of MnS_2O_6 in the solution one day, two days, and so forth, later. We found that the manganous dithionate is also decomposed while standing, though this takes place much more slowly at ordinary temperatures than during boiling.

We ran tests to study the completeness of manganese extraction as the result of treating pyrolusite sludges with sulfur dioxide. We started with a Mn/SO_2 ratio ranging from 1:1.4 to 1:1.6, and got only 72-75% extraction of the manganese. We therefore decided to use a much higher excess of SO_2 (over the theoretical value) in our subsequent tests and to subject the sludge (or ore) to repeated sulfur-dioxide treatment.

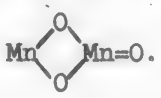
The experimental conditions were as follows: temperature = 80°; Mn/SO_2 ratio = 1:2.9; solid:liquid = 1:10; SO_2 concentration = 13.98%; fineness of grind = 900 openings/cm^2. The first leaching (lasting 90 minutes) yielded 94.12%; the second (lasting 45 minutes) yielded another 1.54%. Thus, double extraction yielded about 96% of the manganese.

The results of these last tests indicate that sulfur dioxide must be used in excess to obtain complete extraction of the manganese from manganese sludges and ores.

Treating Manganite Ores with Sulfur Dioxide

A manganese ore that consists principally of $Mn_2O_3 \cdot H_2O$ is called manganite. This ore usually contains impurities: sand, clay, and other gangue. It is easily turned to a powder owing to its extraordinary softness, so that it is entirely converted into a sludge when washed [40].

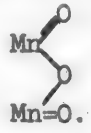
It should be noted that opinions differ regarding the structure of manganese sesquioxide. Some [41,42] consider manganese sesquioxide Mn_2O_3 to be a salt of manganous acid, with the following structural formula:



Others [43,44] consider it to be an oxide of trivalent manganese. When determining the equilibrium constant of the reaction:

$$2Mn^{\cdots} \rightleftarrows Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot}$$

in sulfuric acid, they found that changing the acidity of the solution greatly affected the magnitude of the normal potentials and hence the equilibrium constants [44]. Zanko and Stefanovsky [45], Sem [46], Krull [47] and others, who consider the manganese in Mn_2O_3 to be trivalent, assign it the following structural formula:



In one of our investigations we ran experiments with synthetic manganese sesquioxide, which we treated with sulfuric acid [48]. We found that about half of the substance dissolved, the other half being thrown down as MnO_2. The reaction between dilute sulfuric acid and manganese sesquioxide was represented by the following simple equations:

$$\begin{aligned} &Mn_2O_3 \rightarrow MnO + MnO_2 \\ &MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O \\ \hline &\text{In sum: } Mn_2O_3 + H_2SO_4 \rightarrow MnSO_4 + MnO_2 + H_2O \end{aligned} \qquad (6)$$

To convert the manganese dioxide precipitate into $MnSO_4$ we had to treat it with sulfur dioxide. Hence, the treatment of manganite ores requires the use of a combination method: first treating it with sulfuric acid, and then treating the residue with sulfur dioxide. It would be considerably simpler, of course, if we could confine the treatment to sulfur dioxide alone, without preliminary roasting.

Our tests were run in the apparatus described above.

The reaction between Mn_2O_3 and SO_2 in an aqueous medium may be represented as follows:

$$Mn_2O_3 \rightarrow MnO + MnO_2$$
$$MnO + SO_2 \rightarrow MnSO_3$$
$$MnO_2 + SO_2 \rightarrow MnSO_4$$

In sum: $$Mn_2O_3 + 2SO_2 \rightarrow MnSO_3 + MnSO_4 \quad (7)$$

or

$$Mn_2O_3 + 3SO_2 \rightarrow MnSO_3 + MnS_2O_6 \quad (8)$$

$MnSO_3$ adds oxygen and is converted into $MnSO_4$, while the manganous dithionate that is formed decomposes under suitable conditions into manganous sulfate and sulfur dioxide.

Effect of various factors upon the extraction of manganese from manganite ores or sludges. In these experiments we used manganite ores Nos. 5 and 6, the first sample (" grainy ore") containing 48.55% Σ Mn, 41.88 MnO_2, and 1.56% moisture, and the second sample ("smooth ore") containing 50.08 Σ Mn, 44.52% MnO_2, and 1.11% moisture.

10 g of the ore was used in all the tests. In tests not otherwise specified we used Sample No. 5.

The results of our experiments on the effect of temperature upon the extraction of manganese are shown in Fig. 5.

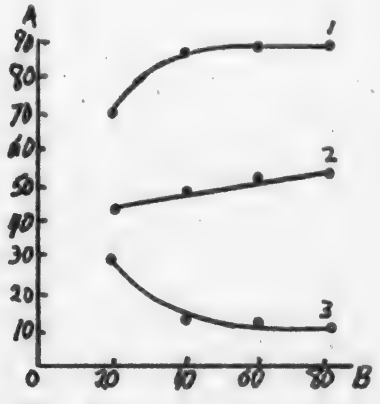


Fig. 5. Effect of temperature upon the extraction of manganese from manganite ores.

Experimental conditions: Time-80 min; solid: liquid = 1:10; fineness of grind - 256 openings/cm²; SO_2 concentration - 13.98 - 14.98%; quantity of SO_2 - 5 liters; A-manganese dissolved, %; B-temp. °C. 1-$MnSO_4$; 2-Σ Mn; 3-MnS_2O_6.

As we see in Fig. 5, raising the temperature from 20 to 80° increases the extraction of manganese (Σ Mn), but only slightly. As the temperature rises, the amount of manganous dithionate formed drops sharply, the quantity of manganous

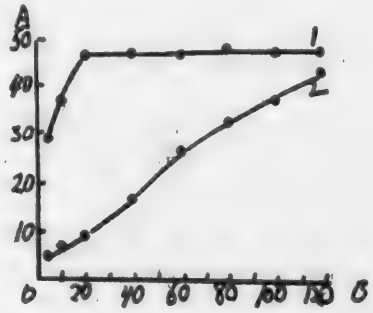


Fig. 6. Effect of time upon the extraction of manganese from pyrolusite and manganite ores.

A-Manganese dissolved, %; B-time, min. 1-Pyrolusite ores; 2-manganite ores.

sulfate rising accordingly. We have taken 80° as the optimum temperature.

The data on the effect of time are listed in Table 7.

The data on the effect of time upon the extraction of manganese from pyrolusite and manganite ores under identical conditions are compared in Fig. 6.

TABLE 7

Effect of Time Upon the Extraction of Manganese from Manganite Ores
Experimental conditions: Temp. = 80°; solid:liquid ratio = 1:10; fineness of grind = 900 openings/cm^2; SO_2 concentration = 14-15.70%; quantity of SO_2 = 5 liters

No.	Time, minutes	Manganese dissolved	
		grams	per cent
1	5	0.2746	5.65
2	10	0.3505	7.22
3	20	0.4474	9.21
4	30	0.6217	12.30
5	40	0.8637	17.79
6	60	1.3468	27.74
7	80	1.6365	33.72
8	100	1.8065	37.21
9	120	2.1241	43.71

TABLE 8

Effect of Fineness of Grind upon the Extraction of Manganese from Manganite Ores
Experimental conditions: Temp. = 80°; solid:liquid ratio = 1:10; SO_2 concentration = 14-15.70%; quantity of SO_2 = 5 liters; time 30 min.

No.	Fineness of grind, openings/cm^2	Manganese dissolved	
		grams	per cent
1	64	0.4174	8.59
2	121	0.5546	11.42
3	256	0.6261	12.89
4	400	0.7147	14.72
5	900	0.8697	17.91
6	2500	0.8951	18.43

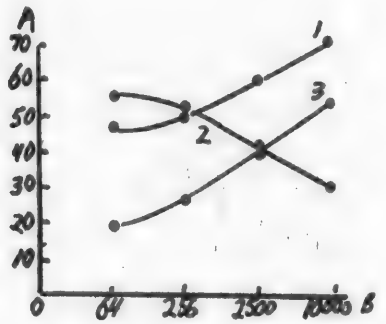


Fig. 7. Effect of fineness of grind upon the formation of manganous dithionate and sulfate.

Experimental conditions: Temp. - 80°; time - 30 min.; solid:liquid - 1:10; SO_2 concentration - 15.04 - 15.19%; quantity of SO_2 - 5 liters. A-% manganese dissolved; B-fineness of grind, openings/cm^2. 1-MnS_2O_6; 2-$MnSO_4$; 3-ΣMn.

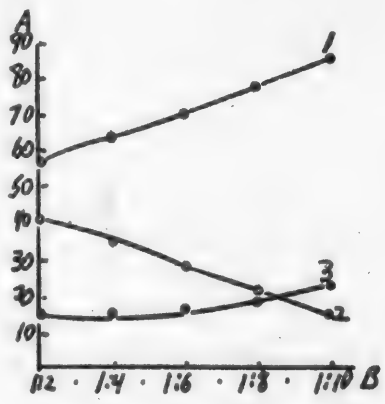


Fig. 8. Effect of the ratio of solid and liquid phases (solid:liquid) upon the extraction of manganese from manganite ores.

Experimental conditions: Temp. - 80°; time-60 min; fineness of grind - 900 openings per cm^2; SO_2 conc. - 13.0-14.16%; quantity of SO_2-5 lit.; A-% Mn dissolved; B-solid:liquid; 1-$MnSO_4$; 2-MnS_2O_6; 3-ΣMn.

The results of the tests shown in Fig. 6 indicate that as time continues the extraction of manganese from manganitic ores rises gradually and uninterruptedly.

Comparison of the data on the extraction of manganese from pyrolusite ores and manganite sludges shows that manganite ores react much more slowly with sulfur

dioxide than do pyrolusite ores and sludges. Much more time is required for the process with the former.

The comparatively low rate of extraction of manganese from manganite (as compared to pyrolusite or braunite) has led some research workers to believe that it must first be roasted [11]. The results of our tests on the effect of the fineness of grind are given in Table 8.

We also made tests (with Sample No. 6 of manganite ore) to determine the effect of grain size upon the formation of manganous dithionate and sulfate. The corresponding data are shown in Fig. 7.

Experimental conditions: Temperature = 80°; time = 30 minutes; solid:liquid ratio = 1:10; SO_2 concentration = 15.04-15.19%; amount of SO_2 = 5 liters.

The test results show that fineness of grind promotes the extraction of manganese from manganite ores; moreover, the coarser the grind, the more manganese sulfate is formed, and, conversely, the finer the grind, the more of the dithionate is extracted.

The tests on the effect of the ratio of the solid and liquid phases (solid: liquid) are shown in Fig. 8.

Varying the solid:liquid ratio from 1:2 to 1:10 increases the extraction of the manganese. The effect of the ratio of the solid and liquid phases on the dissolution of the manganese is largely due to the fact that sulfur dioxide reacts with manganese oxides in the liquid phase. When little water is present, only little sulfur dioxide dissolves, and that little quantity reacts with the manganese sesquioxide in the manganite ore; the rest of the sulfur dioxide is unable to react with the manganese. As the dilution of the suspension is increased, the sulfur dioxide dissolves in the increasing quantities of water, and reacting with the ore, yields a higher extraction of the manganese.

Dilution is a factor that lowers the percentage of manganous dithionate in the solution, as was the case with the pyrolusite sludges.

The data on the tests run to ascertain the effect of concentration are shown in Fig. 9.

As we see, increasing the SO_2 concentration aids in the extraction of the manganese. The higher the concentration of SO_2, the lower the concentration of the entrained inert gases, the less SO_2 will be carried off, and the more of it will be dissolved in the suspension. This raises the useful efficiency of the sulfur dioxide and the extraction of the manganese rises accordingly.

The experiments indicate that more of the manganous dithionate is formed at low concentrations of sulfur dioxide, with relatively less of the manganous sulfate; the latter predominates, however, at higher concentrations of the gas.

Figure 10 shows the data on the effect of the quantity of SO_2 upon the process in question.

The test results have shown that

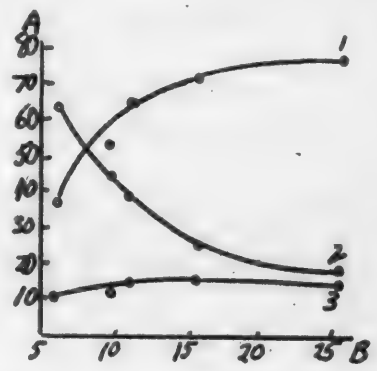


Fig. 9. Effect of SO_2 concentration upon the extraction of manganese from manganite ores.

Experimental conditions: Temp.-80°; time-60 min.; solid:liquid - 1:10; fineness of grind-900 openings/cm²; weight of SO_2 passed through the solution was the same in all runs. A-% manganese dissolved; B-SO_2 concentration,%. 1-$MnSO_4$; 2-MnS_2O_6; 3-Mn.

increasing the quantity of SO_2 passed through (both volumetrically and gravimetrically) increases the manganese extraction. Comparison of the effect of the quantity of SO_2 upon the extraction of manganese from pyrolusite sludges and manganite ores indicates that the degree of manganese extraction is higher for the former than for the latter, all other conditions being the same.

Even various types of manganite ore behave differently when treated with sulfur dioxide. As we see from a comparison of the data (for otherwise identical conditions), the degree of manganese extraction from Sample No. 6 ("smooth ore", Fig. 7) is higher than from Sample No. 5 ("grainy" ore, Table 8). Hence, the structure and the composition of the treated ores have a definite effect upon their behavior; the presence of foreign impurities likewise affects their behavior.

Increasing the quantity of sulfur dioxide passed through, and lengthening the treatment time, causes the quantity of manganous dithionate to drop, while the quantity of manganous sulfate rises.

We then ran tests to determine the completeness of extraction of the manganese from manganite ores. We used Sample No. 5 in these tests. The ore was treated three times with sulfur dioxide, the latter being used in excess (in Test No. 1, the Mn/SO_2 ratio was 1:1.9).

The test results are given in Table 9.

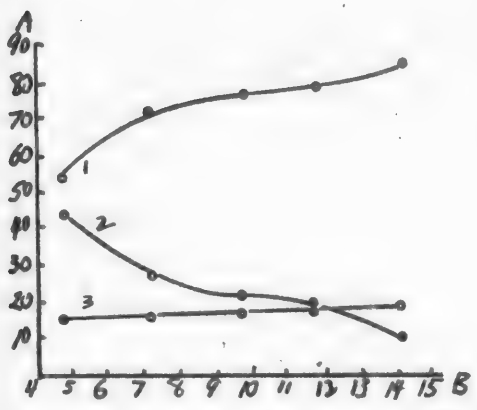


Fig. 10. Effect of quantity of SO_2 upon the extraction of manganese from manganite ores.

Experimental conditions: Temp.-80°; solid:liquid - 1:10; fineness of grind-900 openings/cm²; SO_2 concentration-18.7%. The gas was passed through at a constant rate of flow. A-% manganese dissolved; B-amount of SO_2 passed through, liters.

1-$MnSO_4$; 2-MnS_2O_6; 3-ΣMn.

TABLE 9

Extraction of Manganese from Manganite Ores by Triple Extraction with an Excess of SO_2

Experimental conditions: Temp. = 80°; solid:liquid ratio = 1:10; fineness of grind = 256 openings/cm²; SO_2 concentration = 16.21-17.62%

No.	Time, in min.	Amount of SO_2 passed through, liters	Manganese dissolved	
			grams	per cent
1	100	22	3.7760	77.77
2	50	10	0.4935	10.16
3	30	8	0.0838	1.72
				89.65

As these data indicate, the aggregate extraction of manganese as the result of triple treatment of manganite ore with sulfur dioxide is 90%. The rate of manganese extraction is raised still higher when counterflow extraction is employed.

Thus, all the manganese present in extractable form in manganite ore can apparently be extracted by treating the ore with sulfur dioxide, it merely requiring more time than the corresponding treatment of pyrolusite sludges and ores.

As we see, manganite ores (or sludges) may be utilized both by concentrating them by thermal oxidation (converting them into manganese dioxide with active properties) [49] and by treating them with sulfur dioxide.

When sulfuric acid is cheap and plentiful, and sulfur dioxide is available,

combination method may be employed: treating manganite ores first with sulfuric acid and then treating the residue (MnO_2) with sulfur dioxide [48].

SUMMARY

1. Manganese sludges of the pyrolusitic type (or similar ores) react readily with sulfur dioxide, producing a completely satisfactory extraction of the manganese within a brief space of time.

2. The effects of temperature, time, fineness of grind, solid:liquid ratio, and sulfur-dioxide concentration and quantity upon the formation of manganous sulfate and dithionate have been established.

3. It has been found that various kinds of manganite ore behave differently when treated with sulfur dioxide. The so-called "smooth ore" is most easily treated with sulfur dioxide.

4. When cheap and plentiful sulfuric acid is available in addition to the sulfur dioxide, the combination method may be employed: treating the manganite ores with sulfuric acid, and then treating the precipitated MnO_2 with sulfur dioxide.

LITERATURE CITED

[1] Welter et Gay-Lussac, Ann.chim et phys., 10, 312 (1819).

[2] C.Schorlemmer, A Treatise on Chemistry, 1, 457 (1911).

[3] V.Antony, Gazz. chim.ital., 32, 1, 514 (1902).

[4] J.Meyer, Ber., 34, 3606 (1901).

[5] F.Meyer, Ber., 35, 3429 (1902).

[6] H. Carpenter, J. Chem. Soc., 81, 1 (1902).

[7] L.Marino, Z. anorg.Chem., 56, 233 (1908).

[8] F.Meyer and W. Schramm, Z. anorg. allgem. Chem., 13, 226 (1923).

[9] T.Dymond and F.Hughes, J. Chem. Soc., 71, 314 (1897).

[10] E.Davis. Dissol. of Various Manganese Minerals. U.S.Bureau of Mines, 3024 (1930).

[11] E.Leaver. Hydrometallurgy of Manganese. U.S.Bureau of Mines, 6770 (1934).

[12] D.Liddel, Handbook of Non-Ferrous Metallurgy, 11, 1271 (1926).

[13] German patent 39106.

[14] U.S.Patent 1348068.

[15] U.S.Patent 1304222.

[16] German Patent 390043.

[17] Canadian Patent 216019.

[18] German Patent 505584.

[19] Austrian Patent 1230/31.

[20] W.Chamford, Trans. of American Inst. of Mining a. Mettalurg. Eng., 112, (1935).

[21] U.S.Patent 2000211.

[22] C.Basore and E.Eilang, Alabama Polytech. Inst. Bull., Eng. Exp.Sta., 7, (1935).

[23] French Patent 836287.

[24] A.Kirsanov and Yu.Klimenko, J.Appl. Chem. 8, 7, 1152 (1935).

[25] A.Kobakhidze and T.Amokadze, Trans. Tbilisi Inst. Chem., Georgian Branch, USSR Acad.Sci., 1, 1935.

[26] S.Ramkhilevich, G.Voinilovich, and E.Yarovinskaya. Author's Certificate 1985 (issued in 1937).

[27] K.Goldberg, Org. Chem. Ind., 6, 21, 23 (1937).

[28] K.Krivoruchko Minerals Dressing J., 2, 14 (1938).

[29] R.Agladze, Mining Journal, 12, 39 (1939).

[30] R. Agladze, Technique (in Georgian), 1939, 7-8-9, 95.

[31].R.Agladze, Bull. USSR Acad. Sci., 1942, 1-2, 45.

[32] V.Kakabadze, Technique (in Georgian), 1939, 7-8-9, 80.

[33]. V.Kakabadze, Bull. Mendeleev All-Union Chem. Soc., 4, 32 (1940).

[34] V.Kakabadze, Anotated Reports, III Scientific and Engineering Conf., Georgian Industrial Inst., 56 (1940).

[35] Enrichment of Manganese Sludges, 22, Inst. Chem., Georgian Branch, USSR Acad. Sci. (1940).

[36] Yu.Klimenko and A.Kvaskov, Technical News, 7, 13-14, 33 (1940).

[37] Yu.Klimenko and A.Kvaskov. The Chemical Enrichment of Manganese Ores. Metallurgy Press (1943).

[38] I.Peisakhov and B.Chertkov, J. Chem. Ind., 10, 6 (1940).

[39] The Chemical Analysis of Manganese Ores and Products of Their Treatment. Inst. Chem., Georgian Acad. Sci., Tbilisi (1942).

[40]. S.Chikhelidze. Mineral Resources of the Georgian Soviet Republic, 448 (1933).

[41]. F.P.Treadwell. Treatise of Analytical Chemistry (Russ. Ed.), I, 148-161 (1931).

[42] B.Franke, J.prakt.Chem., 36, 451 (1887).

[43] J. Meyer and R.Kanters, Z. anorg. allgem. Chem., 185, 172 (1930).

[44] Grube and Huberich, Z. Elektrochem., 28, 8 (1923).

[45] A.Zanko and V.Stefanovsky, J. Appl. Chem. 9, 12, 2192 (1936).

[46] Sem., Z. Elektrochemie, 27, 426, (1915).

[47] F.Krull, Z. anorg. allgem. Chem., 208, 134 (1932).

[48] V.Kakabadze. Bull. Georgian Indust. Inst. 2 (16), 47 (1945).

[49] V.Kakabadze, Trans. Georgian Indust. Inst., 1 (15), 397 (1943).

THE FRACTIONATION OF CELLULOSE FROM CUPRAMMONIUM SOLUTIONS

N. V. Shulyatikova and D. I. Mandelbaum

All-Union Synthetic Fiber Research Institute

As we know, celluloses with identical chemical characteristics may often behave quite differently during their processing into synthetic fibers. Present methods of analysis fail to give a complete picture of the quality of cellulose. The development of new methods of describing cellulose ought to facilitate an improvement in its quality, in accordance with the task facing the synthetic-fiber industry: creating the most efficient technological processes for the production of hydrated cellulose fibers and for increasing the strength of the latter. Our research had as its objective a study of the polydispersion of cellulose. Apparently, the nature of the distribution of the macromolecules according to size, the so-called polydispersion, is of considerable importance in determining the properties of cellulose in the preparation of synthetic fibers or films.

Various fractionation methods have been employed to define the polydispersion of cellulose. All the known methods of fractionation can be divided into two groups: 1) methods based upon the fractional dissolution of cellulose or of its derivatives in solvents of different composition; and 2) methods of fractional precipitation of the fractions of cellulose or of its derivatives from solutions in various solvents.

Methods involving the fractionation of cellulose esters (acetylcelluloses, nitrocelluloses) are widely employed [1-7].

One of the disadvantages of the methods of determining the polydispersion of cellulose that involve the preparation of its derivatives is the possibility of different substitutions for its hydroxyl groups during the process of esterification, which results in a classification according to degree of esterification as well as according to the size of the macromolecules during fractionation.

When this is so, the degree of polymerization of the fractions, as well as their quantitative yield, is not a function of the chain length alone [8]. Moreover, it should be borne in mind that destruction cannot always be entirely prevented during the production of cellulose esters [4].

The method of fractionating cellulose described in the literature, which involves its successive treatment with a solution of 10% caustic soda as the temperature is gradually reduced [8], does not make it possible adequately to define the heterogeneity of the cellulose materials with a high degree of polymerization, owing to the low solubility of natural cellulose in a 10% solution of caustic soda, (below 30%).

The method of alkaline fractionation, moreover, does not yield reliable results, inasmuch as cellulose is extremely sensitive in an alkaline medium to the action of atmospheric oxygen, the destruction being especially noticeable in the

high-molecular fractions. This method may be used to fractionate hydrated cellulose fibers, where the cellulose has a lower degree of polymerization.

A method involving fractional dissolution in phosphoric-acid solutions of gradually increasing concentration (at 20° C) [10] has also been suggested for determining the polydispersion of cellulose. Our preliminary investigations, as well as the researches of Ekenstam [10], have shown it is difficult to fractionate cellulose with phosphoric acid because of the considerable swelling of cellulose in that acid, which interferes with its separation into fractions by filtration.

Another disadvantage of this method is the possibility of hydrolytic cleavage of the cellulose during its dissolution in phosphoric acid at 20°C. The latter circumstance has been confirmed in a number of papers [11].

Besides the methods set forth above, we must also deal with the methods involving the fractionation of cellulose from cuprammonium solutions. We know that various celluloses dissolve completely in a cuprammonium solution with suitable percentages of copper and ammonia, no matter what their degree of polymerization.

Neiman, Rogovin, and Obogi [9], Gaas [12], Kumichel [13], and others have demonstrated experimentally that it is possible to dissolve cellulose fractionally in cuprammonium solutions containing a low percentage of copper. Battista [14] conducted fractionation by fractionally precipitating the several cellulose fractions from cuprammonium solutions at 0° in an oxygen atmosphere.

The suggested methods of fractionating cellulose from cuprammonium solutions are either difficult to perform, however, or they do not characterize the polydispersion of the cellulose adequately, owing to the extent of its destruction during dissolution and the regeneration of the fractions.

It is the objective of the present paper to work out a practical method for the fractionation of cellulose that makes it possible to secure comparable characteristics of the polydispersion of various cellulose samples.

EXPERIMENTAL

In developing a method for the fractionation of cellulose from cuprammonium solutions we have successively investigated the different factors that might affect the results of fractionation.

Testing the solubility of various samples of sulfite viscose cellulose in cuprammonium solutions whose copper concentrations varied from 0.65 to 1.0% indicated that increasing the percentage of copper in the solution increased the solubility of the cellulose. The insoluble portion of the cellulose swelled up only slightly and could be filtered out without difficulty.

Effect of temperature upon the dissolution of cellulose in cuprammonium solutions. The dissolution of lint at 20°C in air involves considerable destruction of the cellulose; this destruction is much less pronounced at 0° C (Table 1).

Effect of the duration of treatment with cuprammonium solution upon the solubility of cellulose. The fractional dissolution of cellulose in an inert gas atmosphere is practically complete within an hour, the solubility of the cellulose exhibiting almost no change during any ensuing prolonged treatment (Table 2).

Destruction of cellulose during dissolution in cuprammonium solution in an atmosphere of nitrogen. As our tests have shown, the cellulose macromolecules are destroyed when cellulose is dissolved in cuprammonium solution in air (at 20 and 0° C) (Table 3).

TABLE 1

Effect of Dissolution Conditions Upon the Results of Fractionating Cellulose From Cuprammonium Solutions
Initial Degree of Polymerization of Lint = 1060

Conditions under which lint was dissolved	Regeneration conditions	Per cent composition of cuprammonium solution	Per cent cellulose in initial sample		Degree of polymerization	
			Test 1	Test 2	Test 1	Test 2
20° C, in air	100% acetic acid at 0° C	1.3% copper, 15% ammonia	100.1	100.08	490	710
0° C, in air			99.83	100.04	854	890

The cellulose was then dissolved in cuprammonium solution in an atmosphere of purified nitrogen in order to eliminate this destruction. The sample of cellulose was subjected to evacuation ten times, alternating with filling with nitrogen, and the supply of solution to the dissolving vessel was so arranged as to exclude the entrance of air. Dissolution was effected at 20° C, with constant stirring for 1 hour; the hydrated cellulose was regenerated in 10% acetic acid at 0° C.

TABLE 2

Effect of Duration of Treatment with Cuprammonium Solution upon the Solubility of "Viscose No. 5" Cellulose

Duration of treatment	Per cent solubility	
	Test 1	Test 2
1 hour	39.2	41.2
3 hours ...	41.1	39.6

Dissolution of cellulose in an atmosphere of purified nitrogen was employed for our subsequent fractional dissolution of cellulose in cuprammonium solutions containing a constant 15% of ammonia and percentages of copper that ranged from 0.5, 0.6, and 0.7 to 0.8%.

Our experiments on the fractional dissolution of cellulose indicate that the degree of polymerization of the undissolved residues rises progressively; this

TABLE 3

Dissolution of Cellulose in Cuprammonium Solution in an Atmosphere of Purified Nitrogen
Degree of Polymerization of the Original Cellulose: 840

Per cent composition of the cuprammonium solution		Insoluble residues		Fractions	
Cu	NH_3	Quantity, %	Degree of polymerization	Quantity, %	Degree of polymerization
0.5	15	66.93	960-980	27.57 26.3	500-514 530-520
0.6	14.9	29.88	1100-1100	29.35 35.03	536-540 540-520
0.7	15.1	5.6	-	28.83	680-680 740-740

regular rise in the degree of polymerization is not always observed in the succeeding fractions, however. Apparently, this is due to the fact that the method we have adopted of dissolving the cellulose in an atmosphere of purified nitrogen

does not entirely prevent the inclusion of traces of oxygen [15], which causes the destruction of the dissolved portions of the cellulose, especially when the high-molecular portions of the latter enter solution. Using various antioxidants (glucose, sodium sulfite, and cuprous chloride) to bind the traces of oxygen during the dissolution of cellulose in cuprammonium solutions were not very successful.

Effect of the bath factor upon the solubility of cellulose in cuprammonium solutions. When a sample of cellulose is fractionally dissolved in cuprammonium solutions with gradually increasing percentages of copper, it is hard to allow for the bath factor in each successive treatment of the undissolved residue. A special study of the effect of the bath factor upon the solubility of cellulose in cuprammonium solutions has shown that failing to allow for this factor may lead to false results in the fractionation of cellulose (Table 4).

We see in Table 4 that with a high bath factor we were able to dissolve nearly all the cellulose in cuprammonium solutions of various compositions, but with a low percentage of copper. What is important in the dissolution of cellulose in cuprammonium solutions is not only the concentration of copper in the solution, but the total copper present, which is required for the formation of the copper-cellulose coordination compound. This quantity of copper varies for cellulose molecules, depending on their chain length. Thus, we can fractionate cellulose according to the size of its macromolecules by changing the bath factor when dissolving cellulose in cuprammonium solutions containing a low percentage of copper.

TABLE 4

Effect of the Bath Factor upon the Solubility of Cellulose in Cuprammonium Solutions

Percentage composition of the solution		Bath factor	Per cent cellulose	
Cu	NH_3		Undissolved residues	Fractions
0.41	14.8	1:200	1.8 0.58	93.0 94.9
0.31	14.9	1:200	54.02 53.85	37.0 37.2
0.31	14.9	1:500	0.3 0.7	94.3 93.0
0.2	15.1	1:500	68.7 74.1	25.1 18.4

When this fractionation principle is employed, the successive fractional dissolution of a single initial sample of cellulose is complicated. We resorted to the method of fractionally dissolving a series of parallel samples of cellulose, each of them being successively treated with a cuprammonium solution of the same composition, but with a gradually increasing bath factor.

As the bath factor is raised, the soluble portion of the cellulose increases, this portion including the previous fractions that were secured at lower dissolution factors.

This method possesses several advantages over the method involving the successive fractional dissolution of cellulose in cuprammonium solutions with gradually increasing percentages of copper; the principal one is that each fractional dissolution is done according to a strictly defined bath factor.

As has been pointed out above, part of the dissolved cellulose undergoes oxidative destruction when cellulose is dissolved in cuprammonium solutions.

The undissolved residues undergo practically no destruction when acted on by cuprammonium solutions containing little copper. For example, lint with an initial degree of polymerization of 880-900 was treated with a cuprammonium solution of the following composition: 0.26% Cu and 15% NH_3, the bath factor being 1:30. The undissolved residue represented 97% of the weight of the lint and had

a degree of polymerization of 891-899.

With this in mind, we made use of nothing but experimental data on the magnitude of the undissolved cellulose residues and their degree of polymerization in developing our method for fractionating cellulose. The quantity and the degree of polymerization of the dissolved portions and the individual fractions can be calculated, starting with the fact that the mean degree of polymerization of cellulose (as determined viscosimetrically) is the mean weighted value of the figures for the degree of polymerization of all the fractions [16-17].

An analysis of artificial mixtures of cellulosic materials with various degrees of polymerization (Table 5) confirmed this supposition.

TABLE 5

Analysis of Artificially Prepared Mixtures

Initial cellulosic materials	Degree of polymerization	Concentration ratio, %	Mean degree of polymerization of cellulose	
			Calculated	Experimental value
Cellulose No. 5	810	33.3	642	626
Cellulose No. 1	808	33.3		
Viscose Rayon	310	33.3		

Our method of fractionating cellulose was worked out on the basis of these investigations.

The method is founded upon the fractionatinn of cellulose by fractinnally dissolving it in a cuprammonium solution containing a low percentage of copper, the bath factor being varied during dissolution. Fractionation was carried out at 0° C (thawing ice) in air.

Description of the method of fractionating cellulose. The following reagents were employed: 1) a cuprammonium solution constituted as follows: 0.25-0.26% Cu, 15.0-15.2% NH_3; 2) 10% acetic acid; and 3) 15% aqueous ammonia.

Before fractionation, the cellulose sample was stirred for 5-10 minutes in an aqueous medium with a concentration of 1% by means of a propeller stirrer (3000 rpm). Then the cellulose was suction-filtered through linen on a filter funnel and dried in air at room temperature to a moisture content of 7-9%. The moisture in the cellulose was determined before fractionation.

This preparatory treatment of average cellulose samples is very important for the securing of reproducible results in fractionation.

One-gram samples of cellulose (containing 7-9% moisture) were placed in 500-ml dark-glass jars, which were tightly closed by stoppers through which the stirrers passed via an oil seal.

Then dissolution was effected in the corresponding quantity of cuprammonium solution (depending upon the bath factor) for 2 hours at 0° C, with constant stirring by the stirrer (80 rpm). Both the cellulose and the cuprammonium solution had been chilled to 0° C in advance. When dissolution was complete, the undissolved residues were vacuum-filtered out through densely woven perchlorovinyl cloth (Artikul 130). The residues were washed three times with a 15% solution of ammonia, using 25 ml for each washing; then two to three times with distilled water, and two to three times with 10% acetic acid; then the residues were washed with distilled water until their reaction was neutral. The washed residues were lifted off the filter with tweezers and transferred to a tared box. The were dried to constant weight at 105°, and the quantity of undissolved residue was

determined in per cent of the original sample.

Similar fractional dissolutions were effected to determine the specific viscosities, the undissolved residues being dried in air at room temperature to an air-dry state. Part of each undissolved residue was used to measure the moisture content, the rest serving in the determination of the specific viscosities of 0.05% cuprammonium solutions of cellulose.

The specific viscosities were measured in an atmosphere of purified nitrogen.

The degree of polymerization of the undissolved residues was computed from Staudinger's formula:

$$P = \frac{\eta_{sp}}{C \cdot 10 \cdot K_m},$$

where $K_m = 5 \cdot 10^{-4}$.

Thus, by varying the bath factor in the dissolution of parallel samples of celluloses in a cuprammonium solution containing a low percentage of copper (Table 6) we get a series of undissolved cellulose residues, with different weights and degrees of polymerization.

The number of fractional dissolutions may be varied at will, depending upon the need for securing a more or less detailed picture of the polydispersion of the unknown sample of cellulose.

With the experimental data on the quantity and degree of polymerization of the undissolved residues, we can calculate the amount and degree of polymerization of the dissolved portions of the cellulose and then those of the individual fractions, from the equations:

$$DP = \Sigma M_x \quad DP_x \quad \text{and} \quad DP_{initial} = DP_A \cdot M_A + DP_a \cdot M_a,$$

where $DP_{initial}$ is the mean degree of polymerization of the initial sample of cellulose; DP_A is the degree of polymerization of the undissolved residue A in the cellulose under test; M_A is the amount of the undissolved residue A; $\overline{DP}_a$ is the degree of polymerization of the dissolved portion a; and M_a is the amount of the dissolved portion a.

We have fractionated several samples of sulfite cellulose of various brands by the method described above.

We reproduce the integral and differential distribution curves of macromolecule size for five samples of cellulose (Figs. 1 and 2).

		DP
Sulfite cellulose, enriched	No. 1	844
	No. 2	988
	No. 3	848
Sulfite cellulose, not enriched	No. 4	818
	No. 5	840

When we compare the results of fractionating these cellulose samples, we note that the enriched celluloses Nos. 2 and 3 contain a negligible amount of low-molecular fractions. The maximum on the distribution curves is located in the region of high degrees of polymerization (600-1000), especially in Cellulose No. 2, which has a high mean degree of polymerization.

The poorly enriched cellulose No. 1 has a large percentage of high-molecular fractions, together with a considerable amount of low-molecular fractions; the differential distribution curve does not exhibit a maximum in the region of the fractions that interest us most, with a mean degree of polymerization in the 600-800 range.

The nonenriched, though highgrade, celluloses Nos. 4 and 5 have similar

TABLE 6

Data on the Fractionation of Cellulose

Cellulose samples	Bath factor	Undissolved portion		Dissolved portion		Different fractions	
		Quantity, %	Degree of polymerization	Quantity, %	Degree of polymerization	Quantity, %	Degree of polymerization
Sample No. 1. Degree of polymerization: 844*	1:30	91.25	910	8.8	160	8.8	160
	1:75	81.3	978	18.7	261	9.9	350
	1:125	64.9	1087	35.1	394	16.4	545
	1:175	56.7	1124	43.3	477	8.2	820
	1:225	30.7	1161	69.3	703	26.0	1083
						30.7	1161
Sample No. 2. Degree of polymerization: 988*	1:30	94.5	1033	5.5	215	5.5	215
	1:75	89.8	1074	10.2	231	4.7	249
	1:125	84.9	1108	15.1	313	4.9	483
	1:175	79.6	1148	20.4	379	5.3	567
	1:225	74.2	1190	25.8	454	5.4	737
	1:300	39.9	1318	60.1	768	34.3	1004
	1:350	27.3	1453	72.7	813	12.6	1030
						27.3	1453
Sample No. 3. Degree of polymerization: 848*	1:30	94.6	890	5.4	112	5.4	112
	1:75	88.4	922	11.6	284	6.2	433
	1:125	81.2	958	18.8	373	7.2	516
	1:175	72.7	1012	27.3	411	8.5	612
	1:225	50.9	1088	49.1	599	21.8	834
	1:275	42.0	1124	58.0	648	8.9	918
	1.325	17.1	1240	82.9	767	24.9	1044
						17.1	1240
Sample No. 4. Degree of polymerization: 818*	1:30	93.1	864	6.9	197	6.9	197
	1:75	88.7	883	11.3	219	4.4	253
	1:125	80.3	952	19.7	272	8.4	343
	1:175	68.1	1003	31.9	423	12.2	666
	1:225	25.8	1138	74.7	709	42.8	922
						25.3	1138
Sample No. 5. Degree of polymerization: 840*	1:30	92.2	887	7.8	249	7.8	249
	1:75	86.3	937	13.7	229	5.9	–
	1:125	79.8	965	20.2	346	12.4	406
	1:175	74.8	991	25.2	391	5.0	573
	1:225	36.1	1094	63.9	696	38.7	894
						36.1	1094

*Initial degree.

Notes: 1-The figures for the quantity of undissolved residues are the mean of two parallel tests.
2-The figures for the degree of polymerization of the undissolved residues are the mean of four parallel tests.

similar distribution curves of macromolecule size. The curves display maxima in the region of mean values of degree of polymerization (Table 6).

The distribution curves of macromolecule size may also be plotted without calculating the quantitative percentages of their fractions or their degrees of polymerization, by directly laying off along the axis of ordinates the figures for the quantity and the degree of polymerization of the undissolved residues.

The curves thus plotted also characterize the polydispersion of the cellulose (Fig. 3).

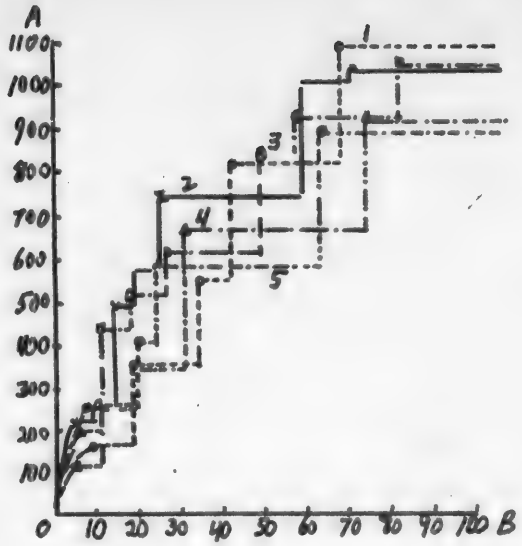


Fig. 1. Integral distribution curves of macromolecule size.

A-Degree of polymerization; B-quantity of cellulose dissolved. 1-Sample No.1,DP - 844; 2-Sample No. 2, DP - 988; 3-Sample No. 3, DP - 848; 4-Sample No. 4; DP - 818; 5-Sample No. 5, DP - 840.

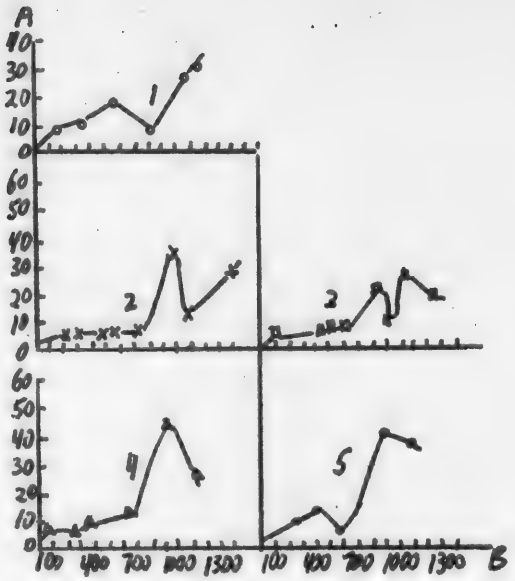


Fig. 2. Differential distribution curves of macromolecule size.

A-Quantity of cellulose dissolved,%;
B-Degree of polymerization.
1-Sample No. 1; 2-Sample No. 2; 3-Sample No. 3; 4-Sample No. 4; 5-Sample No. 5.

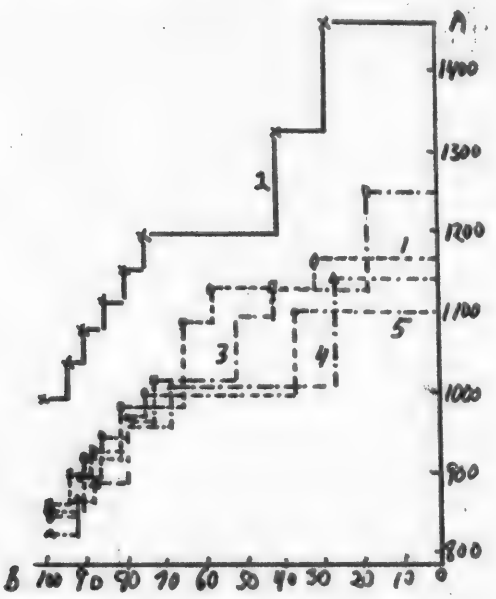


Fig. 3. Integral distribution curves of macromolecule size (from the undissolved residues).

A-Degree of polymerization; B-Quantity of cellulose dissolved. 1-Sample No. 1, DP - 844; 2-Sample No. 2, DP - 988; 3-Sample No. 3, DP - 848; 4-Sample No. 4; DP - 818; 5-Sample No. 5, DP - 840.

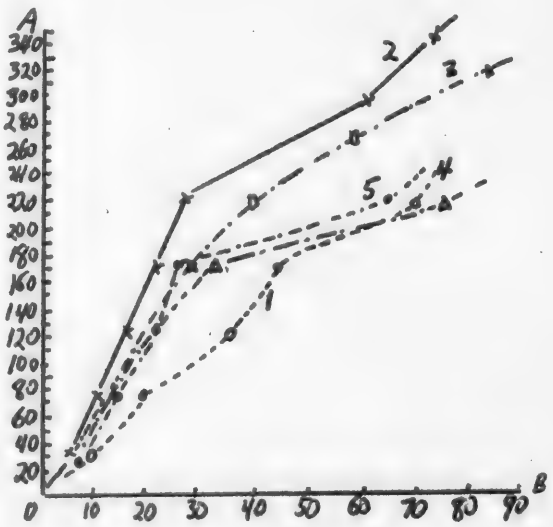


Fig. 4. Effect of the bath factor upon the solubility of cellulose.

A-Bath effect; B-Quantity of cellulose dissolved,%. 1-Sample No. 1, Dp - 844; 2-Sample No. 2, DP - 988; 3-Sample No. 3, DP - 848; 4-Sample No. 4; DP - 818; 5-Sample No. 5, DP - 840.

In some cases we can obtain a rough idea of the nature of the polydispersion of a cellulose by plotting cellulose solubility curves: laying off on the axis of ordinates the values of the bath factors used in dissolving the cellulose in the cuprammonium solution (by the method outlined above), with the quantity of cellulose dissolved laid off along the axis of abscissas. This can be recommended solely for preliminary studies, however (Fig. 4).

The solubility curves for the enriched celluloses, Nos. 2 and 3, rise steeply, indicating their negligible content of low-molecular, readily-soluble fractions.

The poorly enriched cellulose, No. 1, yields an uneven curve, without the rise that characterizes enriched celluloses. This cellulose contains a large percentage of fractions that are soluble at low bath factors. The curves of the nonenriched celluloses, Nos. 4 and 5, manifest large plateaus in the region of medium solubilities, which indicates the high homogeneity of these celluloses.

SUMMARY

1. A study of the solubility of cellulose in cuprammonium solutions has shown that cellulose can be fractionated according to macromolecule size from cuprammonium solutions cnntaining low percentages of copper.

2. A study of the effect of the bath factor upon the dissolution of cellulose in cuprammonium solutions that contain a low percentage of copper has shown that the total quantity of copper necessary for the formation of the copper-cellulose coordination compound, as well as the absolute concentration of copper in the solution, is important in the dissolution of cellulose in a cuprammonium solution.

Varying the bath factor during the dissolution of cellulose in cuprammonium solutions that contain a low percentage of copper makes it possible to fractionate cellulose according to size of the macromolecules.

3. Fractinnal dissolution of cellulose at 0° C in cuprammonium solutions containing a low percentage of copper has shown that the undissolved residues undergo practically no destruction by the cuprammonium solution during the fractinnation process. The fractions regenerated from the solution do not always exhibit a regular increase in the degree of polymerization; this is apparently due to the fact that the cellulose macromolecules are partially destroyed during the dissolution of the high-molecular portions of the cellulose in the cuprammonium solution as well as during regeneration of the fractions.

4. Our investigations of the fractionation of cellulose from cuprammonium solutions have resulted in the elaboration of a method for fractionating cellulose, based on fractional dissolution in a cuprammonium solution containing a low percentage of copper by varying the bath factor during dissolution.

This method makes it possible to fractionate various samples of cellulose and to plot curves of the distribution of macromolecules according to size. The curves are plotted from the experimental data on the quantity and the degree of polymerization of the undissolved residues.

5. This new method yields reproducible results for parallel fractionation tests and makes it possible to define the polydispersion of unknown samples of cellulose.

LITERATURE CITED

[1] Rogovin and Glazman, J. Appl. Chem., 8, 7 (1935).

[2] A.I.Medvedev, J. Appl. Chem. 6, 5 (1933).

[3] Lachs, Kropmann, Kolloid-Z., 79, 91 (1937).

[4] Staudinger, Ber., 68, 161 (1935).

[5] Badgley, Frilette, Mark, Ind. Eng. Chem., 3-7, 3, 227-232 (1945).

[6] Sookne, J.Research Nat. Bur. Standards., 30, 1 (1949); Ibid., 29, 123 (1942).

[7] Dorr, Kunstseide und Zellwolle, 4, 10 (1940).

[8] Dolmetsch u. Reinecke, Zellwolle, 7, (1939).

[9] Neiman, Rogovin, and Obogi, Org. Chem. Ind., 461 (1936).

[10] Ekenstam, cited by Zibera: Die Chemischtechnischen Untersuchungsmethoden der Zellstoff- und Papier-Industrie (1943).

[11] Schulz, J. prakt. Chem., 157, 238 (1941).

[12] G.Gaas, J. prakt. Chem., 161, 131 (1942)

[13] Kumichel, Der Papierfabrikant, 49, 495-508 (1938).

[14] Battista, J. Am. Chem. Soc., 5 (1946).

[15] O.P.Golova, Bull. USSR Acad. Sci., (1945).

[16] Korshak. Introduction to the Study of High-Molecular Compounds. 85-87 (1946).

[17] Rafikov, Korshak, and Chelnokova, Bull. USSR Acad. Sci., 1949, 1.

Received October 26, 1949.

A COMPARATIVE EVALUATION OF VARIOUS METHODS OF PREPARING TRIHYDROXYGLUTARIC ACID FROM XYLOSE

N. V. Chalov, O. G. Temir, Z. P. Gavrilova and A. I. Kruzhevnikova

All-Union Research Institute of the Sulfite Alcohol and Hydrolysis Industry

In 1932 Prof. Shorygin [1] proposed the employment of trihydroxyglutaric acid as a perfect substitute for citric and tartaric acids in the food industry and other branches of industry.

In view of the shortage of organic nutritive acids and with a view toward the manysided utilization of agricultural plant wastes, the question arose of the industrial production of trihydroxyglutaric acid by oxidizing xylose with nitric acid.

The following methods of preparing trihydroxyglutaric acid are known at the present time: Plyushkin's [2]; Sychev's [3]; and Aizenberg's and Zilberman's [4].

We were assigned the problem of making a comparative evaluation of the various methods and of selecting the one best suited for industrial application. The results of our investigation along these lines are set forth in the present paper. We append a brief description of the different methods of preparing trihydroxyglutaric acid and of their comparative features.

Plyushkin method [2]. The xylose is mixed with nitric acid, sp. gr. 1.20. 160 g of nitric acid is used (in terms of 100% acid) per 100 g of xylose. Oxidation is effected at 90-95° for 2 hours. The oxidized solution is evaporated to a syrup, dissolved in a small amount of water, and again evaporated to a syrup to drive off the nitric acid. Then the syrup is dissolved in 15 times its weight of water, heated to boiling, and neutralized with a precise equivalent of chalk. The calcium oxalate that settles is filtered out. Calcium trihydroxyglutarate separates out of the hot filtrate upon standing. Evaporation in vacuum yields some more of the latter salt.

Sychev method [3]. The xylose is mixed with nitric acid, sp. gr. 1.20-1.25, 160 g of the latter (in terms of 100% acid) being used per 100 g of the xylose. Oxidation is performed for 2 hours at 60°. The oxidized solution is evaporated in vacuum over a water bath to a syrup, after which a small quantity of water is added, and the whole is re-evaporated. The syrup is diluted with water to a sp. gr. of 1.25 and set aside to stand for 12-36 hours for the oxalic acid to crystallize out. The crystals that settle out are separated by centrifuging; then the syrup is diluted with water to a quantity that is 4 times the weight of the xylose used in oxidation and neutralized. Neutralization is done with chalk, in two stages. In the first stage half the equivalent quantity of chalk is added to the solution, heated to 80°, and the whole is stirred for 2-3 minutes. The precipitate of calcium oxalate is filtered out. The filtrate is neutralized at the same temperature, the second half of the equivalent amount of chalk being added to it. Much of the calcium trihydroxyglutarate separates out

of the hot light-brown solution upon standing. The rest of it, amounting to some 12%, is recovered by vacuum evaporation.

Aizenberg and Zilberman method [4]. The xylose is dissolved in water in the proportion of 1:2. The xylose solution is oxidized with nitric acid, sp. gr. 1.40, the proportions being 1:3.5. The concentration of nitric acid should be 250-300 g/liter before oxidation. Oxidation lasts 2 hours at 75-80°. The oxidized solution is diluted with an equal quantity of water, without evaporation, and neutralized in the cold with chalk or lime. Neutralization evolves the precipitation of calcium oxalate, which is filtered out. The filtrate is boiled for 30 minutes; this causes calcium trihydroxyglutarate to settle out. It is filtered out.

All the foregoing methods decompose the calcium trihydroxyglutarate with 20% sulfuric acid to recover the trihydroxyglutaric acid. The solution of trihydroxyglutaric acid is separated from the gypsum, purified with activated charcoal, evaporated, and crystallized.

EXPERIMENTAL

Trihydroxyglutaric acid was produced by each of the methods described above. The comparative indexes of these methods are listed in the table.

Research method. The research was done with commercial xylose, secured from corn cobs.

The commercial xylose contained 89.2% of pure xylose. 200 g of xylose was used in each test for oxidation. The onset of oxidation was indicated by the appearance of brown oxides of nitrogen.

The oxalic acid in the oxidized solution was determined by the Sychev method [3].

In accordance with this method, the oxidized solution was diluted with water and neutralized with chalk at room temperature. The oxalic acid is recovered quantitatively from the solution as its calcium salt. The practical application of the Sychev method has shown that it is best to dilute the solution with water until a ratio of 1:4 is reached, in terms of the xylose used for oxidation. After the oxalic acid has been filtered out, a 25% solution of calcium acetate is added to the filtrate, its quantity exceeding the amount of trihydroxyglutaric acid present by 400 to 500%. Then the solution is heated and boiled for an hour. The precipitated calcium trihydroxyglutarate is filtered out, washed, and desiccated to constant weight. This method has been tested with artificial mixtures. It was found to be wholly satisfactory for analytical purposes, and a correction was applied for the solubility of calcium trihydroxyglutarate.

The nitric acid in the oxidized solution was determined conductometrically. The pH was determined with a lamp potentiometer and a glass electrode.

As our data indicate, the Plyushkin method provides a yield of no more than 36.7% of trihydroxyglutaric acid from xylose. The loss of trihydroxyglutaric acid during the elimination of the oxalic acid is extremely high, amounting to 50%. The Sychev and the Aizenberg-Zilberman methods are nearly equal in point of yield of trihydroxyglutaric acid, the output of trihydroxyglutaric acid by the Sychev method being 7.8% higher than by the Aizenberg-Zilberman method. The Sychev method entails evaporation of the oxidized solution, however, whereas the Aizenberg-Zilberman method does not require that operation, which is a point in favor of the latter. The Sychev method yields 12.6% more of trihydroxyglutaric acid in the form of an intermediate product – the calcium salt – than the Aizenberg-Silberman method. The amount of nitric acid used per 100 g of trihydroxyglutaric acid produced by the Sychev method is only half the consumption by the Aizenberg-

Zilberman method.

It should be noted that evaporation over a water bath does not remove the nitric acid completely, much of it remaining in the syrup.

Comparative Indexes of the Production of Trihydroxyglutaric Acid By Various Methods

Technical indexes of the production of trihydroxyglutaric acid by various methods	Dimensions	Method of production		
		Sychev'	Plyushkin's	Aizenberg's-Zilberman's
A. Oxidation				
Substance oxidized	–	Crystalline xylose	Crystalline xylose	30 N solution of xylose in water
Quantity of nitric acid	g/100 g	160	160	304
Oxidation temperature	°C	90-95	60	75-80
Oxidation time	hours	2	2	2
B. Oxidized Solution After Evaporation and Dilution With Water				
Solution volume per 100 g xylose	ml/100 g	1500	500	1000
Concentration of nitric acid	g/100 ml	1.47	7.69	14.9
Concentration of oxalic acid	g/100 ml	1.05	1.45	1.07
Concentration of trihydroxyglutaric acid	g/100 ml	2.45	10.80	5.02
C. Output of Trihydroxyglutaric Acid				
By analysis of the oxidized solution, referred to the xylose.....	%	36.70	54.00	50.20
In terms of calcium trihydroxyglutarate recovered, referred to the xylose	%	18.20	51.8	46.0
Losses of trihydroxyglutaric acid during its recovery from the solution	%	50.5	4.07	8.40
D. Output of Oxalic Acid				
Output of oxalic acid, referred to the xylose	%	15.75	7.24	10.7
E. Nitric Acid Consumed for Oxidation				
Entered into reaction as per cent of the quantity used for oxidation.....	%	86.3	76.0	50.9
Consumption per 100 g of trihydroxyglutaric acid produced ..	g	436	310	606

In the light of our results, we must conclude that the Sychev method is best suited to industrial application. A final decision must depend, however, upon a sufficiently thorough study of the oxidation process and of the separation of the acids via their calcium salts.

Oxidation of xylose by nitric acid. When xylose is subjected to Sychev oxidation, the evolution of nitrogen oxides comes to a stop after 20-25 minutes have elapsed. But when the oxidized solution is evaporated over the water bath, nitrogen oxides are evolved copiously. This is evidence that the major oxidation process does not take place at 60°, but rather during the enusing evaporation of the oxidized solution. We checked this assumption by making analyses of samples of the oxidized solution taken at fixed intervals of time during the Sychev method of oxidation and subsequent evaporation. Our results are shown in Fig. 1. As we see, only 5% of trihydroxyglutaric acid was formed during two hours of oxidation at 60°, only 32% of the nitric acid having entered into solution. Only when the oxidized solution was evaporated did the trihydroxyglutaric acid begin to be formed, and the quantity of nitric acid entering into the reaction begin to rise. By the time the operation was complete 88% of the nitric acid had entered into reaction, and 52% of trihydroxyglutaric acid had been formed. As the oxidized solution is evaporated, the nitric acid is concentrated in the residue, inasmuch as the vapor contains only 0.84% of the acid, while the liquid contains 20%. Increasing the concentration of nitric acid and raising the temperature to 95-98° causes intensive oxidation, trihydroxyglutaric acid being formed. Hence, the evaporation of the oxidized solution, undertaken by Sychev in order to eliminate the nitric acid, actually is an oxidation process. Moreover, because of the low volatility of nitric acid and the fact that the oxidation reaction comes to a stop after its concentration has reached a certain value in the oxidized solution being evaporated to a syrup, the latter will always contain 10-15% of nitric acid.

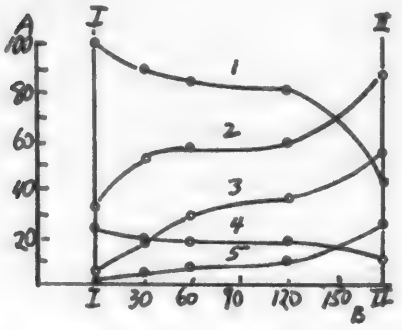


Fig. 1. Indexes of the oxidation of xylose by nitric acid, sp. gr. 1.2, in the Sychev method.

A-% indexes of the process; B-evaporation time over the water bath, minutes.

I-I: Indexes of the xylose oxidation process after 2 hours at 60°; II-II: Indexes of the oxidation process after evaporation by the Sychev method.

1-Change in solution volume during evaporation; 2-Nitric acid entering into reaction, in % of the acid used for oxidation; 3-yield of trihydroxyglutaric acid in % of the xylose; 4-Nitric acid concentration in the evaporated solution; 5-concentration of trihydroxyglutaric acid in the evaporated solution.

When xylose was oxidized by the Plyushkin method, the output of trihydroxyglutaric acid was practically only 2/3 of the output by the Sychev or Aizenberg-Zilberman methods. The only way in which that can happen is for the trihydroxyglutaric acid formed to be destroyed during the process of oxidation. In order to ascertain the reasons for this low yield of trihydroxyglutaric acid we oxidized xylose with nitric acid (sp. gr. 1.2) for 2 hours at various temperatures. In all the runs we used 160 g of nitric acid (in terms of the 100% acid) per 100 g of xylose. Our results are shown in Fig. 2.

As we see, the output of trihydroxyglutaric acid by the Plyushkin method is greatly affected by the oxidation temperature. At 60°, the output of trihydroxyglutaric acid was 5% of the xylose, and that of oxalic acid only 0.9%; when the oxidation temperature was raised to 70°, the output of trihydroxyglutaric acid rose to 24.5%, rising to 32.4% at 80°. At the same time, the nitric acid entering into reaction, which had been 32% at 60°, rose to 55% at 80°. But at 90° the output of trihydroxyglutaric acid dropped to 25%, despite the fact

that the amount of nitric acid entering into reaction had risen to 65% of the acid used for oxidation, while the yield of oxalic acid rose to 8%. The yield of trihydroxyglutaric acid dropped even more sharply when oxidation was carried out at 100°. Hence, the optimum temperature for the oxidation of xylose by nitric acid (sp. gr. 1.2) is 80°. The formation of trihydroxyglutaric acid comes to a stop, however, owing to the drop in the concentration of nitric acid.

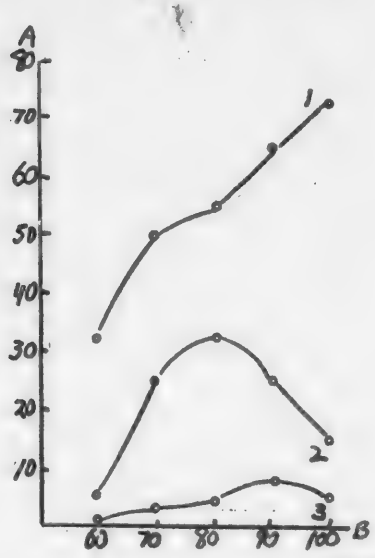


Fig. 2. Indexes of the oxidation of xylose by nitric acid ($\underline{d}$ = 1.2) in 2 hours at various temperatures, 160 g of 100% HNO_3 being used per 100 g of xylose.

A-Values of the process indexes,%; B-Oxidation temperature, °C.

Process indexes: 1-Amount of HNO_3 entering into reaction, in % of the acid used for oxidation; 2-output of trihydroxyglutaric acid, in % of the xylose; 3-output of oxalic acid, in % of the xylose.

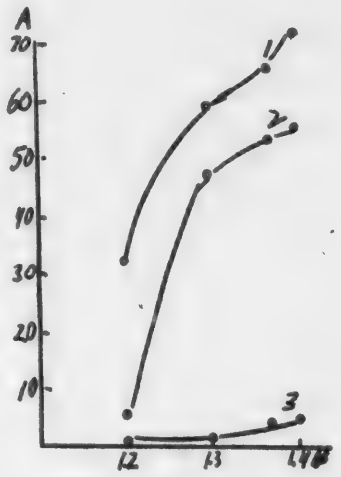


Fig. 3. Indexes of the oxidation of xylose by nitric acid of different concentrations in 2 hours at 60°, 160 g of 100% HNO_3 being used per 100 g of xylose.

A-Process indexes in %; B-Specific gravity of nitric acid.

Process indexes: 1-amount of nitric acid entering into reaction, in % of the acid used for oxidation; 2-output of trihydroxyglutaric acid, in % of the xylose; 3-output of oxalic acid, in % of the xylose.

In the Aizenberg-Zilberman procedure, nitric acid with a sp. gr. of 1.4 is used for oxidation, but inasmuch as the xylose being oxidized is dissolved in water, the concentration of the acid is about 250-300 g/liter when the xylose solution is mixed with the acid, i.e., it is equivalent to a nitric acid with a sp. gr. of 1.2. The amount of nitric acid used is 304 g (in terms of the 100% acid) per 100 g of xylose, i.e., twice as much. This increase in the consumption of nitric acid keeps its concentration in the solution high, thus ensuring a yield of some 50% of trihydroxyglutaric acid. The oxidizing procedure proposed by Aizenberg and Zilberman is uneconomical, owing to the double consumption of nitric acid. It is evident that the consumption of nitric acid for oxidation may be diminished by increasing its concentration. We checked this assumption by oxidizing xylose with nitric acid of different specific gravities. In all the runs 160 g of nitric acid (in terms of the 100% acid) was used per 100 g of the xylose. Oxidation was continued for 2 hours at 60°. The results of the tests are shown in Fig. 3.

As we see, the concentration of nitric acid affects the output of trihydroxyglutaric acid considerably. Increasing the concentration of nitric acid from

32.6% (sp. gr. 1.2) to 47.5% (sp. gr. 1.30) results in a sharp rise in the output of trihydroxyglutaric acid – from 5 to 46.8% of the xylose. Increasing the nitric acid concentration further, to 59.4% (sp. gr. 1.37) and 65.4% (sp. gr. 1.40) raises the trihydroxyglutaric acid yield to 52.4 and 54.5%, respectively.

These figures indicate that all the proposed methods of producing trihydroxyglutaric acid require improvement in their oxidation procedures, and that without this improvement they are unsuited for industrial use: the Aizenberg-Zilberman method because of its high consumption of nitric acid, and the Sychev method because of the need for evaporating the oxidized solution. Our investigations have shown, however, that the Sychev method is the most efficient of all the methods.

In the light of our data, the following improved procedure for the oxidation of xylose by the Sychev method may be recommended: oxidation temperature: 80°; oxidation time, 2 hours; quantity of nitric acid used: 160 g (in terms of the 100% acid) per 100 g of xylose. Concentration of the nitric acid: 50-65% (sp. gr. 1.30-1.40). The procedure suggested by us ensures a steady output of 50-55% of trihydroxyglutaric acid. The percentage of nitric acid entering into reaction will be 63-70%. This amount of the nitric acid is reduced to nitrogen oxides, which can be easily recuperated to produce 50-65% nitric acid again. No evaporation of the oxidized solution is required.

Separation of oxalic and trihydroxyglutaric acids via their calcium salts. All the methods for separating oxalic from trihydroxyglutaric acid are based upon their fractional recovery from solution via their calcium salts, the oxalic acid being recovered first, and the trihydroxyglutaric acid afterward.

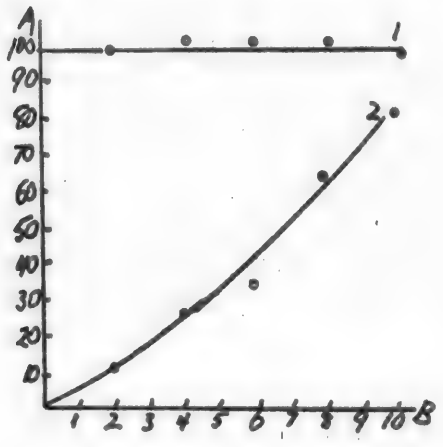


Fig. 4. Separation of oxalic and trihydroxyglutaric acids by the Plyushkin method.

A-Acid recovered from the solution, in % of the initial content; B-neutralization time, min. 1-oxalic acid; 2-trihydroxyglutaric acid.

To ascertain the conditions governing the separation of oxalic acid in the Plyushkin method, we diluted the syrup with water 15 to 1, and divided the resulting solution into 5 parts. Each part of the syrup diluted with water was neutralized with the equivalent quantity of chalk at 100°. The chalk was added all at once with vigorous stirring; then the neutralized solution was kept for 2 to 10 minutes, after which it was rapidly chilled by throwing in a piece of ice and cooling the outside of the flask with water. The precipitate was filtered out, and its percentages of oxalic and trihydroxyglutaric acids were determined. The results are shown in Fig. 4.

As our results show, the Plyushkin method of neutralization does not yield a sharp separation of the oxalic and trihydroxyglutaric acids. Within 10 minutes after neutralization more than 80% of the trihydroxyglutaric acid separates out together with the oxalic acids as their calcium salts. It is evident that this method of separating oxalic and trihydroxyglutaric acids is unsuited for industrial use.

We tested the method of neutralization and separation of the oxalic and trihydroxyglutaric acids proposed by Sychev by diluting the oxidized solution pro-

duced by his method with water after it had been evaporated and then dividing it into 10 parts. Neutralization was effected with half the equivalent quantity of chalk at 80°.

Our results are shown in Fig. 5. As we see, the Sychev method provides an adequately sharp separation of the oxalic from the trihydroxyglutaric acids when the procedure recommended by the author (2-3 minutes of neutralization) is followed. But if the neutralized solution is kept at 80° for 30 minutes, 15% of the calcium trihydroxyglutarate is precipitated together with the calcium oxalate. This indicates that half the equivalent quantity of chalk is excessive. In accordance with Sychev's investigations, we began by adding enough chalk during the first stage of neutralization to neutralize only the nitric and oxalic acids, instead of adding half the equivalent quantity. When this was done, keeping the neutralized solution for 30 minutes caused all the calcium oxalate to settle out, while practically all the trihydroxyglutaric acid remained in solution.

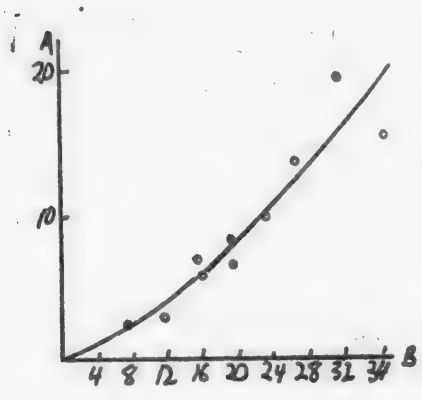


Fig. 5. Separation of oxalic and trihydroxyglutaric acids by the Sychev method during the first stage of neutralization.

A-Trihydroxyglutaric acid recovered from the solution, in % of the initial content;
B-Neutralization time, minutes.

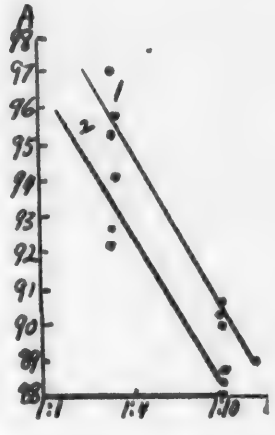


Fig. 6. Recovery of trihydroxyglutaric acid (as its calcium salt) from different dilutions of the oxidized solution with water.

A-% of trihydroxyglutaric acid recovered from the solution; B-Dilution of the oxidized solution with water, in terms of xylose.
1-recovery by the Sychev method; 2-recovery by the Aizenberg-Zilberman method.

According to the Sychev procedure, the partially neutralized solution is subjected to a second neutralization after the oxalic acid has been eliminated. This neutralization is effected at 80° with the other half of the equivalent quantity of chalk. In our investigations we found that the calcium trihydroxyglutarate separates out as soon as neutralization is complete. We found that 52% of the calcium trihydroxyglutarate in the solution separates out when the neutralized solution is allowed to stand for 10 minutes at 80°, that 70% separates out after 20 minutes, 90% after 60 minutes, 94% after 120 minutes, and 95% after 180 minutes.

To increase the completeness of the recovery of calcium trihydroxyglutarate, Sychev evaporated the neutralized solution in vacuum after the bulk of the salt had been recovered, thus recovering another 12% of the calcium trihydroxyglutarate in terms of that already recovered.

In the light of our observations it is apparent that the evaporation of the

neutralized solution may be replaced by keeping it for 2 hours at 80°.

It is possible to remove all the oxalic acid without losing any of the trihydroxyglutaric acid by utilizing the Aizenberg and Zilberman method. This method yields good results in so far as the elimination of the oxalic acid is concerned, and we therefore felt it necessary to make a comparison between it and the Sychev method. Xylose was oxidized by the procedure we have recommended. The oxidized solution was divided into 3 parts, each part being diluted with water as follows: 1:4 of the xylose used for oxidation in Part 1; 1:10 in Part 2; and 1:20 in Part 3. The dilution of Part 1 was that used in the Sychev method, the dilution of Part 2 being that used in the Aizenberg-Zilberman method.

The results are shown in Fig. 6. As we see, the Sychev method ensures more complete recovery of the trihydroxyglutaric acid from the oxidized solution than the Aizenberg-Zilberman method does, the difference amounting to several per cent. Increasing the recovery of the trihydroxyglutaric acid from solution is very important in production. The Sychev method must therefore be considered preferable.

The use of chalk is extremely inconvenient in manufacturing, owing to the violent foaming of the neutral solution; moreover, chalk is a more expensive reagent than milk of lime. When we used milk of lime to separate the acids by the Sychev method, the results obtained were the same as when chalk was used for neutralization. The output of trihydroxyglutaric acid by the Aizenberg and Zilberman method was reduced when milk of lime was used for neutralization. We neutralized an oxidized solution (1:10 dilution of xylose) with milk of lime to various pH values in order to determine the optimum conditions for neutralization.

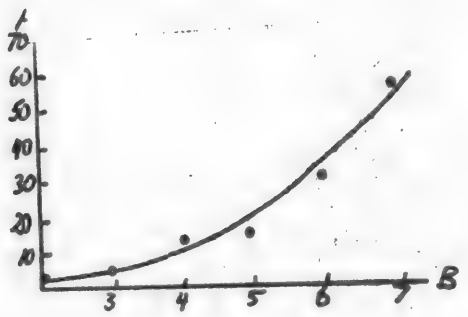


Fig. 7. Recovery of trihydroxyglutaric acid from solution by neutralization with milk of lime at 25-30°, as a function of the pH.

A-% of trihydroxyglutaric acid precipitated together with the oxalic acid; B-pH of the neutralized solution.

Our results are shown in Fig. 7. As we see, the pH of the neutralized solution should not exceed 3.0 when milk of lime is used for neutralization in the cold; otherwise the trihydroxyglutaric acid begins to settle out of the solution together with the calcium oxalate.

Our investigations show that the Sychev method is most advantageous, as ensuring the highest possible degree of recovery of the trihydroxyglutaric acid from the solution.

In conclusion, it should be noted that the method of separating the oxalic acid by neutralizing the oxidized solution in the cold, employed in the Aizenberg-Zilberman method, was suggested by Sychev and described by him as early as 1938. Sychev showed that only calcium oxalate is precipitated when the oxidized solution is neutralized by chalk, even when three equivalents of the latter are used, the trihydroxyglutaric acid remaining in solution. Hence, the method of separating the acids that we have called the Aizenberg and Zilberman method was actually suggested by Sychev, who may claim priority in this respect.

SUMMARY

1. A comparative study has been made of three methods of preparing trihydroxyglutaric acid by oxidizing xylose with nitric acid.

2. The most efficient of the methods investigated is the Sychev method, which yields a high output of trihydroxyglutaric acid for small outlays of auxiliary materials.

The Plyushkin method is unsatisfactory because of its low yields of trihydroxyglutaric acid and the inefficient procedure employed for separating the organic acids via their calcium salts. The Aizenberg and Zilberman method is not quite good enough, owing to the high consumption of nitric acid it requires for oxidation, its lower yield of trihydroxyglutaric acid than in the Sychev method, and its less effective procedure for recovering the trihydroxyglutaric acid from the oxidized solution.

3. None of these methods satisfies optimum requirements in respect to the oxidizing procedure. Our investigations have shown that it is best to oxidize the xylose with nitric acid (sp. gr. 1.35-1.4) for 2 hours at 60°. The amount of nitric acid used should be 160 g (in terms of the 100% acid) per 100 g of xylose. This procedure ensures the highest and steadiest yield of trihydroxyglutaric acid. In its consumption of nitric acid for oxidation and in the temperature and duration of the reaction, this procedure is the same as the oxidation procedure employed in the Sychev method, differing from the latter in the higher concentration of nitric acid used and in the omission of any evaporation of the oxidized solution.

4. Of the methods described, the Sychev method is most efficient as far as separation of the organic acids via their calcium salts is concerned. According to our investgations, the first stage of neutralization should not be performed with half the equivalent quantity of chalk or milk of lime, computed in terms of the total acids contained in the solution, but rather with a quantity that is equivalent to the content of the nitric and oxalic acids in the solution alone. Under these conditions the oxalic acid is completely precipitated from the solution as its calcium salt, the trihydroxyglutaric acid remaining in solution. It is best to perform the first stage of neutralization at 80-100°, and the second stage at 100°, as Plyushkin did.

In conclusion the authors wish to express their gratitude to Prof. N.A. Sychev for his advice during the course of this research.

LITERATURE CITED

[1] P.P.Shorygin. The Chemistry of Carbohydrates. 61. State Technical Press (1932).

[2]. E.Z.Plyushkin. J. Appl. Chem., 1934, 6, 1004-1007; Oils and Fats 3, 37-39 (1934).

[3] N.A.Sychev, J. Appl. Chem., 1938, 1, 68.

[4] V.N.Aizenberg and M.S.Zilberman, Author's Certificate No. 60288, issued by the USSR Peoples Commissariat of the Food Industry, 7 May, 1941.

Received May 22, 1950.

AN INVESTIGATION OF SOME CORROSION INHIBITORS

S. A. Balezin and S. K. Novikov

Several studies have been made of formaldehyde as a corrosion inhibitor [1,2]. The present authors, in particular, have investigated its action in various concentrations of sulfuric and hydrochloric acids [3]; no one had ever noticed any anomalies in the behavior of formaldehyde as an inhibitor, however.

The research was conducted with steel plates made of 0.18% carbon steel. The plates were cleaned with fine emery cloth, degreased with ether, and plunged into the test solutions, which were at rest. The tests were run at room temperature (16.5-18.5°) for 24 hours in 5 N sulfuric acid (chemically pure). Each test was repeated 8 times. The plate's loss in weight was computed in g per m^2 per hour.

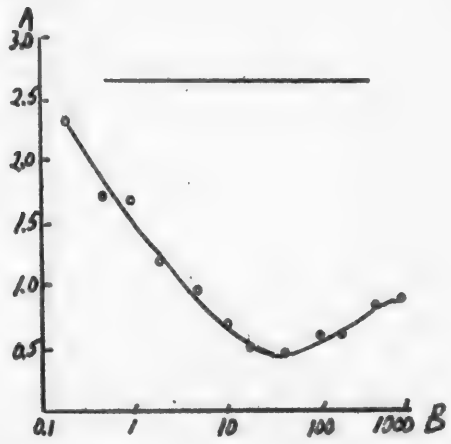


Fig. 1. Rate of dissolution of steel in 5 N sulfuric acid with formaldehyde present.

A-Dissolution rate, g/m^2/hr.; B-concentration of formaldehyde, millimols/liter.
Upper line: acid with no inhibitor present.

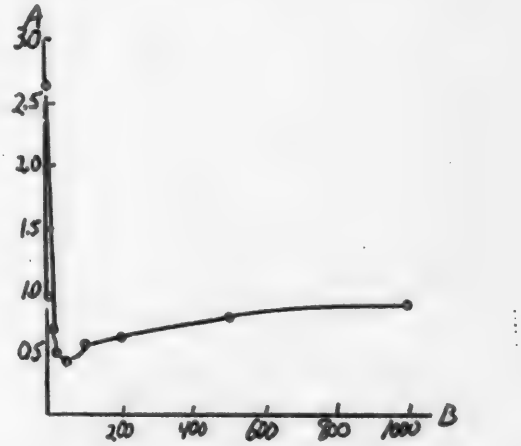


Fig. 2. Rate of dissolution of steel in 5 N sulfuric acid with formaldehyde present.

A-Dissolution rate, g/m^2/hr.; B-concentration of formaldehyde, millimols/liter.

Our test results are shown in Fig. 1, the formaldehyde concentration being plotted logarithmically along the axis of abscissas. The rate at which the steel dissolves in pure acid is shown as a straight line. Part of the results have been also plotted on a normal scale in Fig. 2.

What is striking about these figures is the fact that the curve exhibits

a minimum. The minimum rate of dissolution of the steel is found to occur when only 50 millimols of formaldehyde have been added per liter; any further addition of formaldehyde is not only not useful, but even harmful. This shape of the curve indicates that there are two opposing factors in the solution that affect the rate of dissolution of the steel. One of these factors is obvious: the inhibiting action of the formaldehyde. The higher the concentration of the latter, the stronger its retarding effect. On the other hand, formaldehyde is, as we know, readily reduced by atomic hydrogen to an alcohol [4-7], and as with any oxidant, we see that the dissolution of steel is also stimulated by an increasingly high concentration of formaldehyde.

We made an investigation of the dissolution of steel in 5 N sulfuric acid with 1 mol of formaldehyde in a liter of the solution. We measured the volume of the hydrogen evolved during dissolution, as well as the loss of weight of the steel plate. In pure acid (with no formaldehyde) the two quantities were nearly equivalent, whereas when formaldehyde was present, the volume of hydrogen was only some 40% of the quantity corresponding to the metal's loss of weight. We may therefore consider that 60% of the hydrogen has been consumed to reduce the formaldehyde to an alcohol.

Hence, formaldehyde acts as an inhibitor and as a promoter of the dissolution of steel in sulfuric acid. The stimulating action is especially manifest at a fairly high concentration of formaldehyde in the solution.

Hexamethylenetetramine. Hexamethylenetetramine, first synthesized by Butlerov [8], was suggested as a corrosion inhibitor by Chamberlain in 1929 [9].

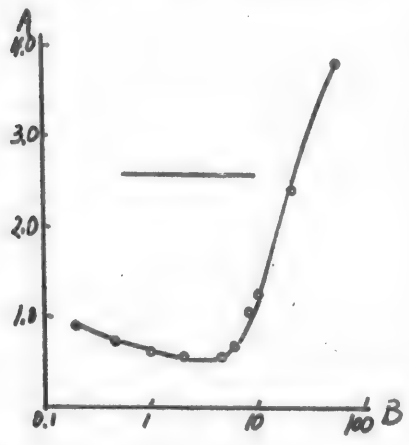


Fig. 3. Rate of dissolution of steel in 5 N sulfuric acid with hexamethylenetetramine present.

A-Dissolution rate, g/m^2/hr.; B-concentration of hexamethylenetetramine, millimols/liter.

Upper line - acid with no inhibitor present.

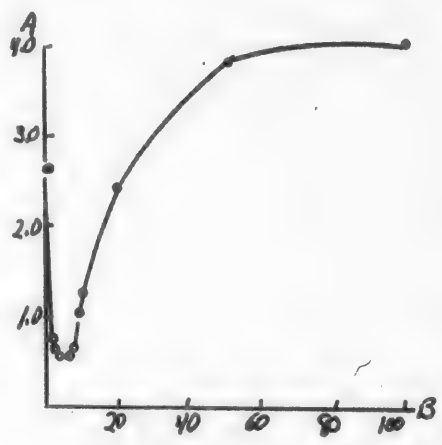


Fig. 4. Rate of dissolution of steel in 5 N sulfuric acid with hexamethylenetetramine present.

A-Dissolution rate; g/m^2/hr; B-concentration of hexamethylenetetramine, millimols/liter.

Hexamethylenetetramine breaks down in an acid medium, the principal products being formaldehyde, ammonia, carbon dioxide, and methylamine [10]. The higher the hydrogen-ion concentration and the higher the temperature, the faster the decomposition of the hexamethylenetetramine [11].

We were interested in testing hexamethyltetramine over a wide range of concentrations. This investigation covered the range from 0.2 to 100 millimols per

liter of solution, the conditions being the same as those for the formaldehyde tests. Each test was run 10 times. The results of these tests are shown in Figs. 3 and 4, the abscissas being logarithmic in Fig. 3 and on the natural scale in Fig. 4.

The curve of the dissolution rate of steel also exhibits a minimum in this case, of course.

But a comparison of Figs. 2 and 4 shows that the accelerating action is much more pronounced with hexamethylenetetramine than with formaldehyde.

Fig. 4 indicates that the rate at which the steel dissolves is about 1.5 times as great as the rate in pure acid when 50 to 100 millimols of hexamethylenetetramine are added per liter of solution. Hence, at these concentrations, the accelerating effect of hexamethylenetetramine (or, more accurately, of its decomposition products) outweighs its inhibitory effect. It may be that the presence of methylamine in the solution accelerates the formation of formaldehyde.

We also made a study of the initial kinetics of dissolution of steel in pure sulfuric acid (5 N solution) and in the same acid with 5 millimols of hexamethylenetetramine added per liter of solution. In the latter case, the solution was allowed to stand for a long enough time before the test began for the decomposition of the hexamethylenetetramine to have been completed.

This investigation was conducted in accordance with the method suggested by Portevin and his coworkers [12].

A hollow glass cone (a funnel) is fitted with two glass hooks, inside and outside the cone. A steel plate previously cleaned with fine emery cloth and degreased with ether is suspended from the inside hook. The outside hook serves to suspend the cone and the plate from the beam of an analytical balance (replacing the pan) by means of a hair or a paraffined thread. The cone together with the steel plate is immersed in a beaker containing the test solution; the cone is so tilted that its air is displaced by the solution. Then the balance is balanced by means of small weights. With a little practice all this requires less than one minute. We then proceeded as follows. 0.12 mg was removed from the pan containing the small weights, thus disturbing the equilibrium; but the dissolution reaction continues: hydrogen is evolved, and the cone with the plate becomes progressively lighter. The time at which equilibrium is restored is read off on a stop watch, another 0.12 mg is removed, and so forth.

In this manner, the evolved hydrogen reduces the weight of the cone, even bubbles of hydrogen that have not yet left the surface of the metal lightening the weight of the cone. The method is extremely sensitive. We have calculated that in our tests a change of 1 mg in the weight of the cone was equivalent to the evolution of no more than 0.001 ml of hydrogen. The reproducibility of the individual runs is quite satisfactory.

Figure 5 illustrates the results of our investigation of the dissolution of steel in 5 N sulfuric acid: both the pure acid and acid containing 5 millimols of hexamethylenetetramine per liter of solution, at room temperature during the first 2.5 hours.

As we see from the graph, dissolution is not the same in the two acids: in the pure sulfuric acid the rate of dissolution decreases with time, whereas dissolution is accelerated in the acid to which hexamethylenetetramine has been added.

We also investigated the rate of dissolution of steel at different temperatures (20, 40, 60, and 80°) in the pure acid (5 N solution) and in the acid to which 5 millimols of hexamethylenetetramine had been added per liter of solution.

Each test was repeated 5 times. The results of the tests are shown in Fig. 6.

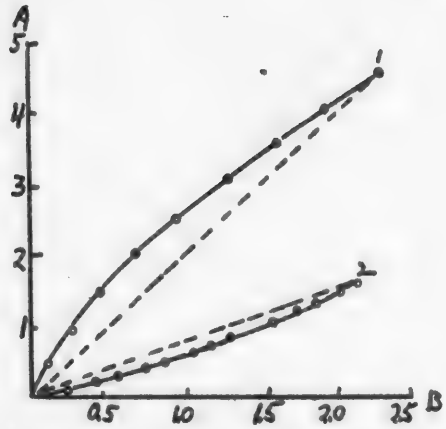


Fig. 5. Evolution of hydrogen during the dissolution of steel in 5 N sulfuric acid: pure acid and acid containing 5 millimols of hexamethylenetetramine per liter.

A-Quantity of hydrogen evolved, in conventional units; B-time, hours.

1-H_2SO_4; 2-H_2SO_4 + $(CH_2)_6N_4$.

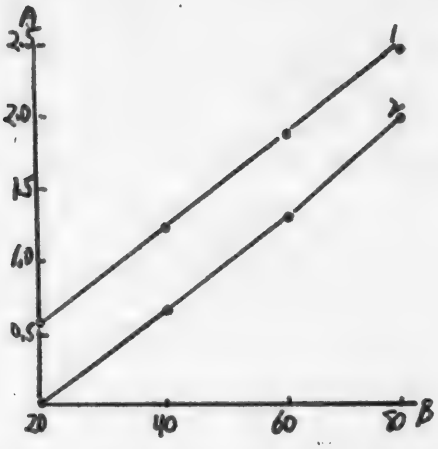


Fig. 6. Variation of the rate of dissolution of steel in 5 N sulfuric acid with temperature: pure acid and acid containing 7 millimols of hexamethylenetetramine per liter.

A-Logarithm of the dissolution rate; B-temperature.

1-H_2SO_4; 2-H_2SO_4 + $(CH_2)_6N_4$.

The temperature coefficient is 2.05 (for 10°) for the pure acid and 2.15 for the acid containing hexamethylenetetramine; i.e., this inhibitor has merely a slight effect upon the temperature coefficient of the rate of dissolution of steel in the acid, which does not agree with the results obtained by Machu [13]. In Machu's opinion, all inhibitors greatly depress the temperature coefficient of the rate of dissolution of steel.

Thiodiglycol. The results of our investigation of the initial kinetics of the dissolution of steel in 5 N sulfuric acid with 30 millimols of thiodiglycol added per liter of solution are shown in Fig. 7. We note that the dissolution rate diminishes with time exactly as in the pure acid, in contrast to the rate of dissolution when hexamethylenetetramine is present (Fig. 5).

We likewise investigated the rate at which steel dissolved at various temperatures (20-80° C) in 5 N sulfuric acid and in the same acid to which 30 millimols of thiodiglycol had been added per liter of solution. Each test was repeated 5 times. The test results are shown in Figs. 8 and 9.

The temperature coefficient (for 10°) is 2.05 for 2 N and 5 N sulfuric acid; it is 1.85 for 2 N acid with thiodiglycol and 2.05 for 5 N acid with thiodiglycol. I.e., the effect of the inhibitor upon the temperature coefficient of the rate at which steel dissolves in the acid is very slight.

Thiodiglycol is a very powerful inhibitor; adding 30 millimols of thiodiglycol per liter to a 5 N solution of sulfuric acid retards the dissolution of steel sixteenfold. In hydrochloric acid, however, thiodiglycol is a very weak inhibitor.

The results of our investigation of the rate at which steel dissolves in 5 N hydrochloric acid with from 1 to 500 millimols of thiodiglycol added per liter

of solution are shown in Figs. 10 and 11. The shape of the curve is evidence that the thiodiglycol is reduced by hydrogen.

When we dissolved steel in sulfuric acid with thiourea, we found that hydrogen sulfide was evolved. Kuznetsov and Iofa [15] found the same to be true of hydrochloric acid.

When steel was dissolved in hydrochloric acid containing thiodiglycol, no hydrogen sulfide was detected in a spot test with sodium plumbite. We assume that the reaction of thiodiglycol with hydrochloric acid is a reversible reaction.

$$S(CH_2-CH_2OH)_2 + 2HCl \rightleftarrows S(CH_2-CH_2Cl)_2 + 2H_2O.$$

The resultant dichlorodiethyl sulfide reacts with atomic hydrogen as follows:

$$S(CH_2-CH_2Cl)_2 + 4H = S(CH_2-CH_3)_2 + 2HCl.$$

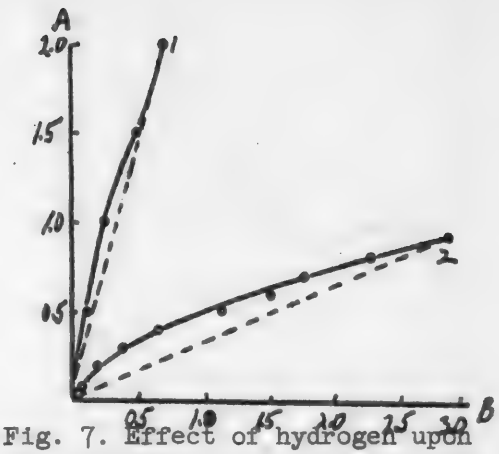


Fig. 7. Effect of hydrogen upon the dissolution of steel in 5 N sulfuric acid: pure acid and acid containing 30 millimols of thiodiglycol per liter.

A-Amount of hydrogen evolved, in conventional units; B-time, hours.
1-H_2SO_4; 2-$H_2SO_4 + S(CH_2CH_2OH)_2$.

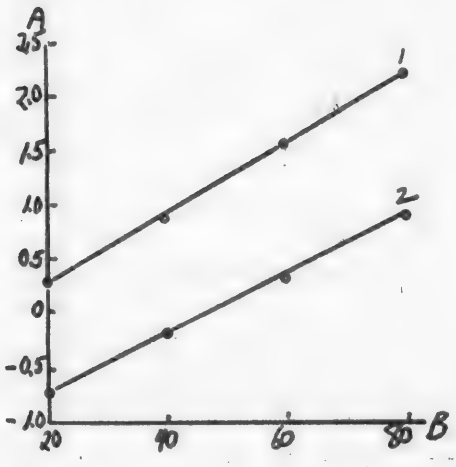


Fig. 8. Variation of the rate of dissolution of steel in 5 N sulfuric acid with temperature: pure acid and acid containing 30 millimols of thiodiglycol per liter.

A-Logarithm of the dissolution rate; B-temperature.
1-2N H_2SO_4; 2-2N $H_2SO_4 + S(CH_2CH_2OH)_2$.

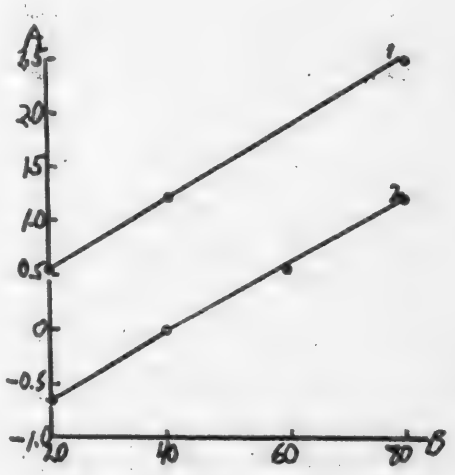


Fig. 9. Variation of the rate of dissolution of steel in 2 N sulfuric acid with temperature: pure acid and acid containing 30 millimols of thiodiglycol per liter.

A-Logarithm of the dissolution rate; B-temperature.
1-5N H_2SO_4; 2-5N $H_2SO_4 + S(CH_2CH_2OH)_2$.

We investigated the dissolution of steel in 0.5 N, 1 N, and 2 N solutions of hydrochloric acid, both the pure acid and acid containing 10 millimols of thiodiglycol per liter of solution, in order to corroborate our interpretation. Each test was repeated 7 times. The results are given in Fig. 12, the retardation factors (γ) being plotted along the axis of ordinates:

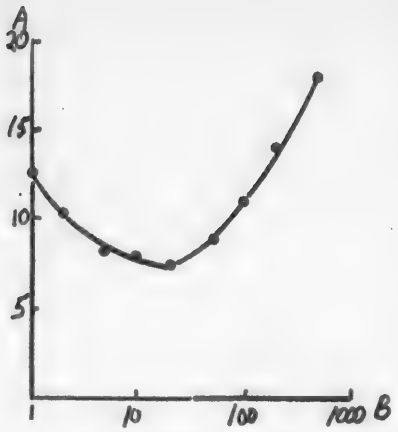


Fig. 10. Rate of dissolution of steel in 5 N hydrochloric acid with thiodiglycol present.

A-Dissolution rate, g/m^2/hr.; B-concentration of thiodiglycol, millimols/liter.

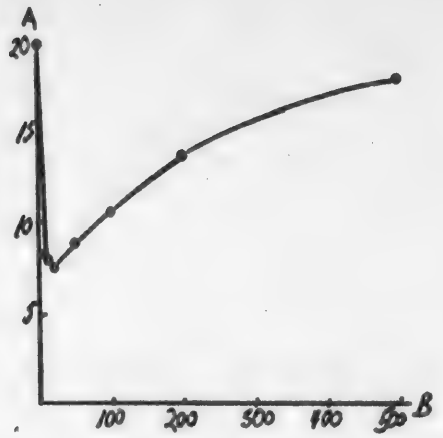


Fig. 11. Rate of dissolution of steel in 5 N hydrochloric acid with thiodiglycol present.

A-Dissolution rate, g/m^2/hr.; B-concentration of thiodiglycol, millimols/liter.

$$\gamma = \frac{\rho 0}{\rho},$$

where $\rho 0$ is the rate of dissolution in the pure acid, and ρ in the presence of an inhibitor. We have shown earlier [3] that when the concentration of the inhibitor is kept constant, the retardation factor rises rapidly as the acid concentration is raised. Fig. 12 shows that the retardation factor in a 1 N acid solution is higher than in a 0.5 N solution, though it drops at concentrations higher than 1 N; this is due to the fact that as the concentration of hydrochloric acid is raised, the equilibrium in the reversible reaction of thiodiglycol with hydrochloric acid is shifted toward the right, i.e., the accelerating effect of the thiodiglycol grows, while its inhibiting action drops sharply. In other words, thiodiglycol acts as both an inhibitor and as an accelerator in hydrochloric acid.

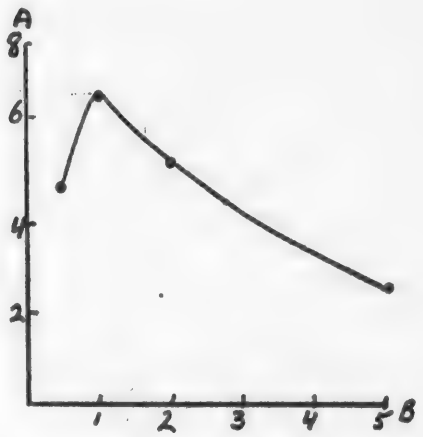


Fig. 12. Variation in the ratardation factor with changes in the concentration of acid, to which thiodiglycol has been added.

A-Retardation factor; B-normality of the acid.

SUMMARY

1. It has been shown that formaldehyde acts not only as an inhibitor, but also as an accelerator of the dissolution of steel in acid. Its accelerating action is especially pronounced when the concentration of formaldehyde in the solution is sufficiently high.

2. It has been shown that thiodiglycol, which is a powerful inhibitor in sulfuric acid, works poorly in hydrochloric acid.

3. It has been found that hexamethylenetetramine and thiodiglycol have very little effect upon the temperature coefficient of the rate of dissolution of steel in sulfuric acid.

LITERATURE CITED

[1] R.Griffin, Ind. Eng. Chem., 12, 1159 (1920).

[2] W.Richardson, Trans. Amer. Electrochem. Soc., 38, 245 (1920).

[3] S.A.Balezin and S.K.Novikov, Sci. Rep., State Polytech. Inst. Moscow, 44, 25 (1947).

[4] Tafel and Schepps, Ber., 44, 2148 (1911); 46, 2564 (1913).

[5] Bredt, J. prakt. Chem., 95, 71 (1917).

[6] Hilbert and Read, J. Am. Chem. Soc., 46, 83 (1924).

[7] Shima, Zbl., 1, 1634 (1926).

[8] A.M.Butlerov, Ann., III, 250 (1859).

[9] U.S.Patent 1719168 (1929).

[10] Hartung, J. prakt. Chem., 46, 1 (1892).

[11] Trenderenburg, Biochem. Z., 59, 146 (1919).

[12] A.Portevin, E. Pretet, L. Guittou, Rev. Metal., 30, 362 (1933).

[13] W.Machu, Korrosion u. Metallschutz, 14, 324 (1938).

[14] S.A.Balezin and S.K.Novikov, Sci. Rep., State Polytech. Inst. Moscow, 44, 62 (1947).

[15] V.A.Kuznetsov and Z.A.Iofa, J. Phys. Chem. 21, 201 (1947).

Received March 24, 1950.

THE EFFECT OF SOLVENTS AND TEMPERATURE UPON THE COPOLYMERIZATION CONSTANTS OF VINYL ACETATE AND MONOMETHYL MALEATE*

S N. Ushakov, S. P. Mitsengendler and B. M. Polyatskina

Chair of Plastics, Lensoviet Technological Institute, Leningrad

In our preceding reports [1,2,3] we have shown that the use of new research methods makes it possible to resolve fundamental problems of copolymerization. Thus, determination of the copolymerization constants σ and μ at 65° enabled us to calculate the composition and structure of copolymers of vinyl acetate and a maleate produced from various compositions of the original mixture and at various depths of transformation.

The plotted diagrams of the differential and integral compositions exhibit the state of the reaction medium at any point in the process. This makes it possible for the research worker to guide the process as he wishes.

The present research had as its objective the determination of the effect of the solvents and the copolymerization temperature upon the copolymerization constants of the system in question.

EXPERIMENTAL

I. Copolymerization in the Presence of Solvents

Investigation of the influence of the solvents upon the size of the constants is of practical as well as theoretical interest. In the system investigated by us, using methanol or acetone, for example, makes it possible to carry out copolymerization in a homogeneous medium. In the copolymerization of vinyl esters with maleic anhydride, which takes place with explosive rapidity, the use of benzene as a diluent reduces the heat of reaction considerably.

This investigation was carried out at 65°, using 0.2% benzoyl peroxide, with a 2:1 ratio of vinyl acetate to the maleate. With such a component ratio the composition of the copolymers hardly changes with the depth of transformation [3]; thus the composition of the copolymers produced under these conditions in various solvents may also serve to some extent as an index of the effect of the medium upon the growth of the macromolecule chain.

We made a study of the effect of both polar (methanol, acetone) and nonpolar solvents (benzene). The standard used was the constant μ for this system, which we determined in a homogeneous mixture at 65°C in methanol [2].

The data in Table 1 show that the composition of the copolymers under homogeneous or heterogeneous conditions** varies but little whether the process is carried out in solvents or without them.

---

* Report IV of a series on the copolymerization of vinyl esters and maleates.

** The copolymers formed do not dissolve in the original mixture or in benzene, but are freely soluble in methanol or acetone.

TABLE 1

Experimental Conditions and Results of Tests of the Influence of Various Solvents On the Composition of the Copolymer and on the Copolymerization Constants

Solvent	Test No.	Vinyl acetate used		Maleate used		Mols of unreacted constituents		Resulting copolymer		% vinyl acetate in the copolymer by weight
		Grams	Mols, V_0	Grams	Mols, M_0	V	M	grams	% of original mixt., wt.	
Without solvent	129	14.9935	0.17434	11.2090	0.086224	0.11958	0.031289	11.851	45.23	39.74
	130	14.2480	0.16567	10.6515	0.081935	0.1107	0.026422	11.9440	47.97	39.58
Benzene	131	8.9640	0.10423	6.6889	0.051453	0.09093	0.03770	2.9313	18.73	39.02
	132	10.7690	0.12522	8.0356	0.061813	0.11539	0.051703	2.1601	11.49	39.16
Acetone	135	9.6452	0.11261	7.1972	0.05536	0.097974	0.040797	3.1856	18.56	39.17
Methanol	73	20.9908	0.2441	15.90	0.1224	0.2302	0.1061	3.29	8.91	36.2
	35	3.10	0.036	2.05	0.0158	–	–	2.8	54.5	41.6

If we insert the experimental values of Table 1 in the integral equation for the Composition (1), solving all the partial equations yields values for the constant μ that are in close proximity (Table 2) for a given value of p, equaling 2.02 (this value of p corresponds to the constant μ for this system, derived by us in methanol at 65°).

TABLE 2

Effect of Certain Solvents Upon the Stability of the Copolymerization Constant μ at 65° and with $VA/M_0 = 2$.

Test No.	Solvent	Composition of copolymer, mol. %		μ	$\Delta\mu$	p
		VA	Me			
129	Without any solvent	49.92	50.08	0.54404	0.00123	2.023
130	Without any solvent	49.76	50.24	0.54011	0.00516	
132	Benzene	49.31	50.69	0.55899	0.01372	
135	Acetone	49.32	50.68	0.55530	0.01003	
73	Methanol	46.20	53.8	0.52790	0.01798	

As we see from Table 2, the discrepancy is greater in methanol as a medium. Still this discrepancy is not large, and may be ascribed to experimental error.

$$\mu = \frac{\log \frac{M_0}{M} - \frac{1}{p} \log \frac{1 - p\frac{V}{M}}{1 - p\frac{V_0}{M_0}}}{\log \frac{V_0}{V} + \log \frac{1 - p\frac{V}{M}}{1 - p\frac{V_0}{M_0}}} \quad (1)$$

* Van Scheidt and Shtraikhman have shown that the physical meaning of the parameter p in Mayo's and Lewis' Equations (1) and (2) is that the value of p represents the composition of an azeotropic mixture (1) in a system where σ and $\mu < 1$.

** V and M – monomers; σ and μ – copolymerization constants.

$$p = \frac{1 - \sigma}{1 - \mu} \cdot \qquad (2)$$

These figures enable us to conclude that for the vinyl acetate – maleate system, whether we carry out polymerization in the mass or in a solvent (methanol, acetone) or with a diluent (benzene) has practically no effect upon the size of the copolymerization constant. This means that the presence of foreign substances does not change the direction in which the chain grows and, hence, does not change the composition of the copolymer.

Our data are in agreement with the figures cited in the literature for the stability of the constants of radical copolymerization when the process is carried out under various conditions and by various methods [4,5]. A change in the composition of the copolymer is taken as an indication of a nonradical reaction.

II. Effect of Temperature Upon the Copolymerization Constants

Temperature is a factor that can affect the growth of the chain, i.e., it may affect the composition of the copolymer. Hence, knowledge of the copolymerization constants of the system at several temperatures is of practical interest, since it gives us an idea of the sensitivity of the resultant polymers to temperature.

Until recently, the copolymerization constants of systems were determined at only one temperature. Only two papers have been published on the measurement of the copolymerization constants at several temperatures with a view to computing the different activation energies in the reactions involving the combination of the radical with both monomers of the system [4,6].

From the Arrhenius equation we may write for μ or σ:

$$\sigma = \frac{K_{V \cdot V}}{K_{V \cdot M}} = P \cdot \underline{z} \cdot \underline{e}^{-\left(\frac{E_{V \cdot V} - E_{V \cdot M}}{RT}\right)} .$$

Knowing the constants for some value of $\underline{T}°$, we can compute the difference $(E_{V \cdot V} - E_{V \cdot M})$ for the reaction of the radical $(V \cdot)$ with its own monomer (V) and with the foreign monomer (M). The more actively the radical reacts with the foreign monomer, the more will σ (or μ) be smaller than unity and the greater will be the difference between the energies of activation of these two reactions. The coefficients preceding the exponential term in the Arrhenius equation represent the steric effect of the reaction. If we start with the concepts of the transition state of the system, the relationship between the reaction rate and the energy of activation for the formation of an activated complex may be expressed by the following equation:

$$K = e^{\frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT}} ,$$

where μ or σ is found to be:

$$\sigma = \underline{e}^{\frac{\Delta S^{\#}_{V \cdot V} - \Delta S^{\#}_{V \cdot M}}{R} - \frac{\Delta H^{\#}_{V \cdot V} - \Delta H^{\#}_{V \cdot M}}{RT}}$$

Measuring the constants at several temperatures enables us to compute the difference in the energy of activation $\left(\Delta H^{\#}_{V \cdot V} - \Delta H^{\#}_{V \cdot M}\right)$ and the difference in the entropy of activation $\left(\Delta S^{\#}_{V \cdot V} - \Delta S^{\#}_{V \cdot M}\right)$ for a reaction involving the combination of a radical with two monomers. The expression $\left(\Delta S^{\#}_{V \cdot V} - \Delta S^{\#}_{V \cdot M}\right)$ indicates the

difference in the steric effects of these reactions.

The calculations made by American research workers, based upon determinations of these constants between 60 and 130° for various monomer pairs, are given in Table 3.

These data indicate that the activity of the monomers is governed principally by the energy of activation. Only in the case of the reaction of the diethyl fumarate radical with styrene is the steric effect important. In the other systems the differences in the entropy of activation (the steric effect) lies well within the limits of experimental error, as may be seen from Table 3.

Table 3 likewise indicates that the temperature coefficient is low, so that the resulting errors in computing the differences in the energy of activation are considerable (50% and more).

TABLE 3

Differences in the Heats and Entropies of Activation in the Copolymerization of Some Monomeric Pairs [4]

Radical	60°	130°	$\Delta H_{11} - \Delta H_{12}$	$\Delta S_{11} - \Delta S_{12}$	$\frac{P_{11}z_{11}}{P_{12}z_{12}}$
Styrene (M_1)	0.520±0.026	0.590±0.026	480±250	0.12±0.68	1.06±0.30
Methylmethacrylate (M_2)	0.460±0.026	0.536±0.026	580±280	0.19±0.76	1.10±0.34
Styrene.....	0.747±0.028	0.825±0.005	380±140	0.54±0.36	1.31±0.16
Methylacrylate ...	0.182±0.016	0.238±0.005	1020±340	0.66±0.86	1.39±0.46
Styrene.....	0.301±0.024	0.400±0.014	1070±320	0.82±0.82	1.5 ±0.5
Diethylfumarate...	0.0697±0.004	0.0905±0.0008	990±290	−2.35±0.73	0.31±0.14
Styrene.....	6.52 ±0.05	5.48 ± 0.56	−660±480	1.87±1.36	2.55±1.26
Diethyl maleate...	0.01	—	—	—	—
Styrene.....	0.742±0.03	0.816±0.015	360±170	0.48±0.43	1.27±0.24
p-Chlorostyrene...	1.032±0.03	1.042±0.015	35±120	0.40±0.32	1.22±0.18

In another published paper [5], the values of the copolymerization constants for three pairs of monomers vary widely even at a single temperature, it being hard to judge the influence of this factor upon the copolymerization constants from this paper: for this reason the energies of activation computed by these authors do not inspire confidence. Their data led the authors to conclude, for example, that the reactions between the sytrene monomer and radicals involve the highest energies of activation. This is contradicted by the experimental evidence on the properties of styrene, which is the most highly active of all the derivatives of ethylene [1].

In our present research we have investigated the effect of temperature upon the constants σ and μ of the vinyl acetate – monomethyl maleate system. We did this by studying the copolymerization of this pair of monomers at 56° and 78°; the interval ordinarily used in practice.

We effected copolymerization without any solvent. The conditions of the experiment run at 56° and the results of analysis are listed in Table 5. The values of σ and μ were computed graphically from the experimental data in Table 5 by means of Equations (1) and (2).

The values of the constants at this temperature were found to be:

$$\mu = 0.47647 \quad \text{and} \quad \sigma = 0.04681 \text{ (Table 4).}$$

TABLE 4

Copolymerization Constants of the System Vinyl Acetate – Methyl Maleate at 56°, As Computed From Equation (1)

Test No.	μ	$\Delta\mu$	σ	$\Delta\sigma$	p
111	0.47510	0.00043	0.04809	0.00128	
113	0.47180	0.00287	0.04290	0.00391	
127	0.47616	0.00149	0.04815	0.00134	1.812
128	0.47563	0.00096	0.04810	0.00129	
Mean value	0.47467	0.00144	0.04681	0.00196	

We determined the constants σ and μ at 78° by running the tests at molar ratios V_0/M_0 of the components that ranged from 2 to 20. Under the conditions employed no noticeable difference was observed in the composition of the copolymers. Only at $V_0/M_0 = 20$ (Table 6, Test 142) did the composition of the copolymer at 24% conversion differ considerably from that of the other copolymers.

The data in Table 6 were used to compute the values of the copolymerization constants. The value of μ is very close to 1 at 78°. Hence, changes in the value of p in Equation (1) have only little effect upon the value of μ. In this range of values of μ, slight fluctuations of its value produce a sharp change in the magnitude of the other constant σ (2), as may be seen in Table 7.

In our case the constant μ was determined by selecting different values of p and inserting them in the composition equation (1). Solving the partial composition equations for a p of 2000 yielded values of μ that differed only in the fifth decimal place.

$$\mu = 0.99956 \pm 0.00002.$$

$$\sigma = -p(1-\mu) + 1 = 0.1168 \pm 0.0458.$$

A comparison of the values of μ and σ at 56 and 78° indicates that a change in temperature over even so small a range greatly affects the copolymerization constants in the system under investigation.

As we see in Table 8, μ and σ increased 2.5 and 2.1 times, respectively, as the temperature was raised by 22°. Hence, raising the temperature increases the activity of both radicals ($V\cdot$ and $M\cdot$) with regard to their "own" type of monomer, at 78° the –V–V– and –M–M– types of bonds predominating in the macromolecule over those formed at 56°. In this interval the ratio of the two constants underwent a minor change (some 10%). This latter circumstance explains the insignificant change in the composition of the copolymers with temperature. As we see from Table 8, the rise in the percentage of vinyl acetate in the 78° copolymer is about 2%.

Knowing the copolymerization constants at 56 and 78° makes it possible to compute in advance the composition and the structure of the copolymers that can be produced at these temperatures for various compositions of the original mixture and various depths of conversion. Calculation of the composition from the approximate equation (3)

$$\frac{V}{V_0} = \left(\frac{M}{M_0}\right)^{\frac{K_a + K_0}{2}} \qquad (3)$$

indicated that all the behavior patterns manifested at 65° are also displayed at 56 and 78°.

Table 5. Conditions and results of Tests run at 56° with 0.3% Benzoyl Peroxide

Test No.	Reaction time, hrs.	vinyl acetate used		methyl maleate used		Mols. of unreacted constituents		V_0/M_0 ratio	V/M ratio	Copolymer produced, grams	Copolymer yield, % initial mix. wt.	Vinyl acetate in copolymer	
		g	mols V_0	g	mols M_0	V	M					% by wt.	Molar %
114	14.0	14.5556	0.16925	10.8700	0.83616	0.1641	0.07847	2.0241	2.0915	1.1088	4.36	39.72	49.90
115	14.7	18.4740	0.21481	13.7970	0.10612	0.1861	0.07657	2.0242	2.4305	6.3126	19.56	39.12	49.27
116	14.3	16.5190	0.19208	5.0150	0.03858	0.1666	0.02094	4.9790	7.9640	4.9070	22.79	44.56	54.85
117	12.7	22.7330	0.26430	6.8933	0.05303	0.2424	0.03340	4.9850	7.2570	4.4382	14.98	42.53	52.80
127	20.0	13.1770	0.15322	4.8998	0.03760	0.1429	0.02848	4.0652	5.0210	2.0773	11.49	42.35	52.61
128	19.0	13.4385	0.15626	4.9971	0.03844	0.1435	0.02696	4.0650	5.3225	2.5912	14.05	42.40	52.67
113	10.0	21.4204	0.24908	3.2162	0.02474	0.2135	0.00463	10.0670	46.090	5.6716	23.02	53.91	63.50

Table 6. Tests run at 78°

121	2.25	11.6740	0.13571	8.7276	0.067135	0.08065	0.01633	2.0215	4.9383	11.3416	55.59	41.77	52.02
122	2.25	11.4220	0.13281	8.5386	0.065683	0.08039	0.01756	2.0220	4.5784	10.7636	53.92	41.88	52.13
123	1.12	11.1120	0.12921	4.1445	0.031881	0.11340	0.01763	4.0527	6.4294	3.2151	21.08	42.39	52.66
124	1.50	10.8685	0.12638	4.0520	0.031169	0.10630	0.01304	4.0546	8.1550	4.0844	27.37	42.28	52.54
125	1.50	11.8350	0.13761	2.9898	0.022998	0.11950	0.00778	5.9836	16.1870	3.5887	24.20	43.43	53.71
126	2.00	12.6670	0.14729	3.2003	0.024618	0.13200	0.01076	5.9831	12.2620	3.1150	19.61	42.19	52.45
142	2.25	40.0910	0.46618	3.0560	0.023508	0.36742	0.00959	19.8310	38.2970	10.3020	23.87	82.44	87.64
145	2.25	13.5990	0.15813	10.1940	0.078415	0.08838	0.01588	2.0165	5.6340	14.1524	59.84	42.38	52.60

TABLE 7

Values of and for a p of 2000 in the Partial Composition Equations in Various Experiments.

Test No.	μ	σ
121	0.99958	0.1600
122	0.99956	0.1200
123	0.99956	0.1200
124	0.99952	0.0400
125	0.99950	0.0000
142	0.99963	0.2600
145	0.99956	0.1200

TABLE 8

Effect of Temperature upon the Copolymerization Constants

Temp., °C	σ	$\frac{\sigma_{t+22°}}{\sigma_t}$	μ	$\frac{\mu_{t+22°}}{\mu_t}$	amt. vinyl acetate in the copolymer under otherwise identical conditions, mol %
56	0.04681	2.49	0.4747	2.1	49.9
78	0.1168		0.99956		52.1

SUMMARY

1. It has been shown that the copolymerization constants σ and μ of the system vinyl acetate – monomethyl maleate are not affected by the presence of solvents.

2. The constants for the system have been computed at 56 and 78°.

3. It has been shown that both system constants are approximately doubled as the temperature is raised from 56 to 78°.

4. Temperature actually effects little change in the composition of the copolymers.

LITERATURE CITED

[1] S.N.Ushakov, S.P.Mitsengendler, and G.A.Shtraikhman, Prog. Chem., 3, 267 (1950).

[2] S.N.Ushakov, S.P.Mitsengendler, and B.M.Polyatskina, J. Appl. Chem. 23, 5 (1950).

[3] Ibid.

[4] F.Lewis, F.Mayo, W.Hulse, J. Am. Chem. Soc., 70, 4, 1519 (1948).

[5] Walling and Briggs, J.Am.Chem.Soc. 72, 1, 48 (1950).

[6] G.Goldfinger, M.Heidlitz, J. Poly. Sci., 3, 5, 786 (1948).

Received May 20, 1950.

See CB translation p. 535 ff.

THE EFFECT OF SLIGHT ALKYLATION

UPON THE PROPERTIES OF CELLULOSE FIBER

N. I. Nikitin and N. I. Klenkova

V. M. Molotov Institute of Technology, Leningrad

Recent researches [1] have shown that hygroscopicity and hydrolyzability may serve as factors largely characterizing the internal state of cellulose structure, the degree of its condensation.

The hygroscopicity of cellulose is governed chiefly by the presence of free hydroxyl groups in it. When the hydroxyl groups are replaced by hydrophobic radicals, the hygroscopicity of the system drops, the magnitude of the drop depending upon the number of such groups introduced. Lorand [2], for example, gives the following figures for the hygroscopicity of several ethers:

	Ethylcellulose	Butylcellulose	Amylcellulose
Degree of substitution, in terms of $C_6H_{10}O_5$	2.15	2.28	1.91
Per cent of water absorbed	3.0	1.673	0.975

A similar picture is obtained for the esters, the hygroscopicity of which likewise drops as the number of carbon atoms in the substituted groups is increased.

A decrease in the hygroscopicity of the cellulose system is observed, however, only when a fairly large percentage of its hydroxyl groups have been replaced. If the degree of substitution is low, i.e., only a few substituent radicals have been introduced into the system, an opposite effect may be produced – the hygroscopicity may be increased. Bletzinger and Aiken [3], for example, made a study of the properties of a paper produced from partially acetylated cellulose and found that the hygroscopicity and the hydratability of the cellulose increased during grinding after a small amount (up to 6%) of acetyl groups had been introduced into it; the mechanical properties of the cellulose sheet produced after such cellulose had been ground were increased accordingly. But when the percentage of acetyl increased beyond the optimum value, the hydrophobic nature of the fiber became increasingly manifest, finally prevailing over the hydration effect.

Jayme and Foundjain [4] have observed a gradual rise in the hygroscopicity of slightly methylated cellulose as the percentage of methyl groups in the latter was raised to 13.6%.

Nikitin, Plekhanova, and Rudneva [5] alkylated alkaline cellulose with methyl iodide vapor and secured low-substituted fiber products that exhibited high hygroscopicity and hydrolyzability.

The introduction of a few hydroxyl groups into cellulose, resulting in an appreciable increase in the latter's hydrophilic properties, is explicable on the assumption that the radicals introduced into the system partially rupture the hydrogen bridges linking the hydroxyl groups of contiguous chains, causing the formation of "fissures" in oriented sections, so that the hydroxyl groups adjacent to the substituted ones can be more freely hydrated. Nikitin's study of the infrared absorption spectra of nitrated cellulose [6] plainly supports this assumption. The spectrograms of partially esterified celluloses exhibit absorption bands that are characteristic of hydroxyl groups not attached by hydrogen bonds, which are not found in natural cellulose. The introduction of bulky radicals, which increase the distance between the chains, establishes steric hindrances to the formation of intermolecular bonds between hydroxyl groups in adjacent chains.

We assume that the increase in the hydrophilic properties of cellulose when a small number of hydrophobic radicals is introduced must rise with an increase in the size of the added radical up to a certain limit, after which the hydrophobicity of the added groups must begin to predominate. Lorand [2], for instance, points out that the introduction of even an extremely small number of benzyl radicals into cellulose is enough to produce a highly water-repellent cellulose system.

EXPERIMENTAL

The principal objective of the present investigation has been tracing the effect of introducing an increasing number of alkyl radicals into fiber cellulose upon the latter's hygroscopicity and hydrolyzability, as an indication of its internal state.

Cotton down (lint) was used as the research object, as being the most accessible representative of natural cellulose capable of exhibiting certain behavior patterns in solving the problems we had set ourselves, owing to the rather high degree of orientation (orderliness) of its internal structure.

Alkylation was effected by reacting the vapors of methyl iodide, ethyl iodide, and ethylene oxide with alkaline cellulose, produced by treating cotton lint with a 17.5% solution of caustic soda and squeezed out to three times its original weight. Treatment with methyl iodide and ethyl iodide was carried out in tightly sealed vats for 22 hours at 50°C. The alkylated alkaline cellulose was washed with dilute acetic acid and with water and air-dried at room temperature. The percentage of methoxy and ethoxy groups was determined by the Vieböck and Schwappach method [7]. The results of our determinations of the hygroscopicity of these low-substituted fiber cellulose systems at various relative humidities of the air (above solutions of sulfuric acid) are listed in Tables 1 and 2 and shown in Figs. 1 and 2.

Because the alkylation process was performed with previously mercerized cellulose, the structure of which differed from that of the original cellulose, the properties of the alkylated samples were studied by comparing them with the properties of a cellulose that had been mercerized under the same alkylating conditions, but without using the alkylating agent, as well as with those of the original cellulose.

We see from the figures in Table 1 and 2 that the mercerization process itself causes a marked increase in the hygroscopicity of cellulose over the figures for the original material. The addition of a few methoxy and ethoxy groups results in even greater hygroscopicity, i.e., expands the fine structure of the cellulose even more, the hygroscopicity increasing with the increase in the extent of substitution. The ethoxy groups introduced into the system are more effective than the methoxy groups, which is probably due to the greater bulk of these radicals.

TABLE 1

Hygroscopicity of Methylated Cellulose

Test material	Hygroscopicity at 15°C: Percentage mositure absorbed at relative humidity of: 100	83.7	68.2	58.3	37.0	16.0	0.5
Original cotton lint	22.6	9.8	7.2	6.7	4.9	2.6	1.2
Cotton lint mercerized with 17.5% NaOH, squeezed out and kept at 50°C for 22 hours	28.1	14.9	10.9	10.4	7.2	4.7	2.1
Methylated lint, containing OCH_3 (in %) 1.2	27.9	14.9	10.7	10.4	6.9	4.9	2.1
1.9	-	15.1	10.6	9.8	6.6	4.2	2.0
3.5	-	15.6	10.5	10.2	6.6	4.4	2.0
7.1	36.2	19.2	13.7	13.1	8.7	4.0	1.2
12.4	-	20.9	15.3	14.1	9.0	4.3	1.3

TABLE 2

Hygroscopicity of Ethylated Cellulose at 19°C

Test material	Per cent moisture adsorbed at relative humidity of: 100	87.7	69.8	40.6	16.4	6.7
Original cotton lint	22.2	12.9	7.9	5.6	2.7	1.7
Cotton lint mercerized, squeezed out, and kept at 50° C for 22 hours.	30.1	15.9	10.7	7.5	-	1.5
Ethylated lint, containing OC_2H_5 (in %) 1.9	30.9	17.9	11.1	8.6	4.8	2.5
3.9	32.2	19.8	12.2	9.4	4.4	2.4
5.9	37.7	20.2	12.9	8.9	3.4	1.2
8.2	38.5	21.1	13.9	9.3	3.5	1.9

Lastly, the swelling of cellulose in alkalies, particularly at low temperatures and when frozen [8], may cause much greater separation of the chains and weakening of the structure during the treatment itself than alkylation under the specified conditions, but the chains will endeavor to come closer together during the washing and gradual drying of the cellulose in order to increase intersaturation of the polar hydroxyl groups. The extent of this rapprochement will be governed mainly by the extent of the disorientation of the system during the swelling process. In the case of alkylation, the rapprochement of the hydroxyl groups in different parts of the system will be hampered by the hydrophobic groups added, which set up steric hindrances to the formation of strong hydrogen bonds, the formation of which is possible at distances not exceeding about 2.8 Å, as spectroscopic investigations have shown.

The effect of introducing methoxy and ethoxy groups upon the hydrolyzability of cellulose is quite characteristic. The cellulose samples were hydrolyzed by boiling them in 5% sulfuric acid for specified periods of time. The amount of fermented sugar in the hydrolyzate was determined by the Bertrand method, recomputed as glucose in per cent of the absolute dry weight of the material hydrolyzed. The results of these determinations are given in Table 3 and Fig. 3.

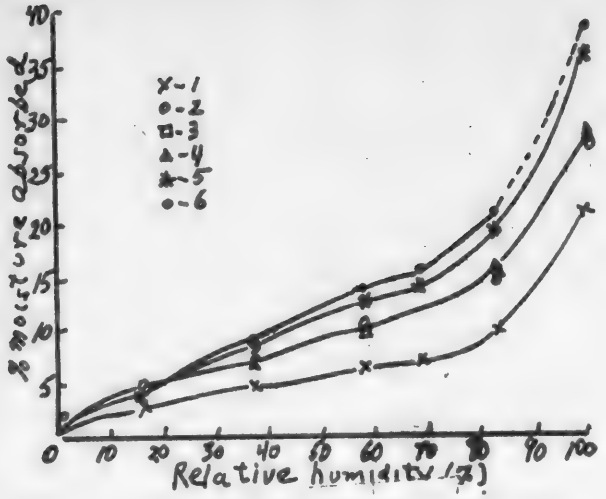


Fig. 1. Hygroscopicity of methylated cellulose at 15° C.

1-Original cellulose; 2-mercerized cellulose; methylated cellulose, containing: 3-1.2% OCH_3; 4-3.5% OCH_3, 5-7.1% OCH_3, 6-12.4% OCH_3.

The figures in Table 3 indicate that introducing a few methoxy and ethoxy groups into cellulose greatly increases the latter's ability to be hydrolyzed, the ethoxy groups increasing the hydrolyzability somewhat less than do the methoxy groups. When a certain degree of substitution is attained, the capacity of the alkylated cellulose for hydrolysis begins to drop, though its hygroscopicity continues to rise. It is quite probable that the attainment of a certain number of alkyl groups establishes a defense of the glucoside bonds, as it were, against the hydrolyzing agent or exerts some sort of influence on these bonds.

In our investigation of the properties of low-substituted methylated and ethylated cellulose samples the following question arose: May not the increase in hygroscopicity and hydrolyzability as the degree of substitution increases be due to the possible destruction of the cellulose bonds during the process of alkylation, and depend upon the quantity of reacting alkyl halide? There is a statement in the literature [5] to the effect that alkyl halides destroy cellulose material. We find another assertion that highly destroyed material possesses high hygroscopicity and hydrolyzability.

We prepared low-methylated samples with different mean degrees of polymerization and different percentages of methoxy groups in order to learn the effect of the degree of polymerization upon the properties of low-substituted samples. We adopted the conventional nitrate viscosity method [9] to determine the degree of polymerization of slightly alkylated samples; we assumed the constant K_m to be $11 \cdot 10^{-4}$ in calculating the degree of polymerization of slightly alkylated celluloses as well as of pure celluloses.

The mean degree of polymerization of methylated and ethylated samples of cellulose, prepared by treating alkaline cellulose with the respective alkyl halides for 22 hours at 50°C, approximated 100. Reducing the alkylation time from 22 to 4 hours and increasing the quantity of alkylating agent yielded a second

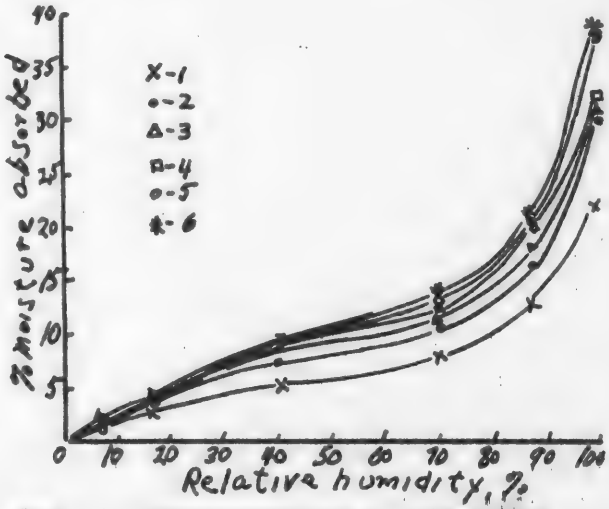


Fig. 2. Hygroscopicity of ethylated cellulose at 19° C.

1-Original cellulose; 2-mercerized cellulose; ethylated cellulose, containing: 3-1.9% OC_2H_5, 4-3.9% OC_2H_5, 5-5.9% OC_2H_5, 6-8.2% OC_2H_5.

TABLE 3

Hydrolyzability of Methylated and Ethylated Cellulose

Material tested		Per cent of substances reduced (glucoses), by weight of the original sample				
		Time of boiling with a 5% H_2SO_4 solution, hours				
		1	2	4	6	9
Original cotton lint		1.5	–	8.0	9.7	–
Linters, mercerized, squeezed out, and kept at 50°C for 22 hours		4.1	10.3	12.2	–	22.0
Methylated cotton lint, containing OCH_3, %	1.6	5.1	10.8	17.5	19.4	28.7
	3.3	9.5	19.5	–	34.1	–
	7.1	21.3	28.4	62.9	–	72.6
	12.8	18.3	22.8	39.8	–	53.6
Ethylated cotton lint, containing OC_2H_5, %	1.9	6.6	9.9	16.2	–	20.9
	3.9	6.5	14.1	23.4	–	40.4
	5.9	–	–	31.3	–	–
	7.8	5.3	–	17.5	–	29.0
	9.5	–	–	14.2	–	–

TABLE 4

Properties of Samples of Slightly Methylated Cellulose

Material tested		Yield after methylation, %	Degree of polymerization	Per cent moisture absorbed, at per cent relative humidity of:			Per cent glucose when boiled with 5% H_2SO_4, 8 hrs.
				81.8	41.1	11.9	
Original cotton lint		–	1360	–	–	–	–
Cotton lint, mercerized, squeezed out, and kept at 50° C for 4 hours		–	400	13.9	8.6	4.8	16.0
Methylated lint, containing OCH_3, %	3.5	–	–	14.0	8.8	4.1	35.5
	3.9	–	–	–	–	–	40.4
	4.5	97.5	420	15.2	9.0	4.8	46.6
	6.7	98.5	380	15.5	10.1	4.5	62.8
	9.6	95.7	405	16.6	10.7	4.1	70.0
	14.6	79.5	410	17.9	10.4	3.7	60.2

series of slightly alkylated samples containing 3.5 to 14.6% methoxy groups, with a mean degree of polymerization ranging from 380 to 420. The results of out tests of the properties of these samples are listed in Table 4.

We produced a third series of slightly methylated samples containing 2.7 to 5.3% methoxy groups and with a mean degree of polymerization of 205 to 240 by treating cellulose, that had been mercerized with a 33% solution of NaOH and squeezed out to four times its original weight, with methyl iodide in acetone. The properties of these samples are given in Table 5.

The difficulty of methylation made it impossible to secure samples with a higher degree of polymerization. Only by using the method recommended by Hess,

Trogus, and their coworkers [10], involving the dimethyl sulfate treatment of a cellulose that had been mercerized and treated with methyl alcohol, did we secure a single methylated sample whose degree of polymerization was 800 and which contained 3.5% of methoxy groups. The hydrolyzability of this sample after 8 hours of boiling with a 5% solution of H_2SO_4 was equivalent to 42.6% of glucose.

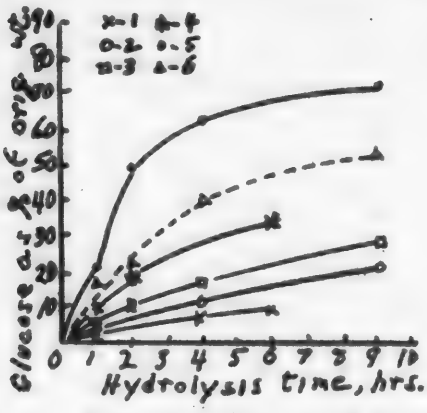


Fig. 3. Hydrolyzability of methylated cellulose.-

1-Original cellulose, 2-mercerized cellulose; methylated cellulose, containing: 3-1.6% OCH_3, 4-3.5% OCH_3, 5-7.0% OCH_3, 6-12.8% OCH_3.

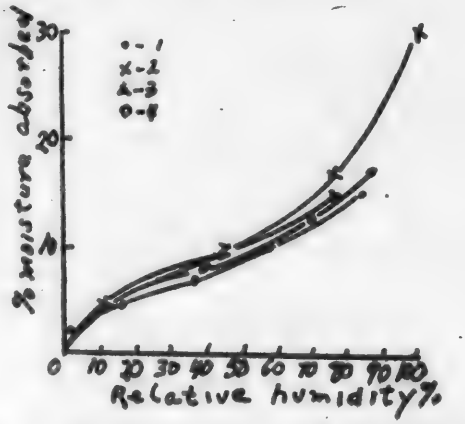


Fig. 4. Hygroscopicity of methylated cellulose of different degrees of polymerization (3.5% methoxy groups).

Degree of polymerization: 1~100, 2~200, 3~400, 4~800

TABLE 5

Properties of Samples of Slightly Methylated Cellulose

Material tested	Yield after methylation, %	Degree of polymerization	Per cent moisture absorbed at 15°C at per cent relative humidity of:				Per cent glucose when boiled with 5% H_2SO_4	
			100	76.6	44.6	11.9	4 hrs	8 hrs
Cotton lint, mercerized and treated under alkylation conditions (but without CH_3I)...	93.6	250	25.5	15.5	9.0	4.3	11.2	17.7
Methylated lint, containing OCH_3, % 2.7	96.4	210	30.3	16.3	9.5	4.3	24.6	26.7
Methylated lint, containing OCH_3, % 4.1	88.4	205	31.3	16.5	9.5	4.0	33.4	45.3
Methylated lint, containing OCH_3, % 5.3	83.4	240	32.2	16.8	9.7	4.3	38.4	52.8

The four methylated samples containing 3.5% of methoxy groups and possessing degrees of polymerization that ranged from 100 to 800 demonstrate that the degree of polymerization has no effect upon the hygroscopicity, by plotting the graphic function reproduced in Fig. 4. The hygroscopicity is plotted along the axis of ordinates for samples with various degrees of polymerization, with the relative humidity plotted along the axis of abscissas. The graph clearly shows that the difference in hygroscopicity for samples with different degrees of polymerization can by no means be explained as due to these differences in degree of polymerization.

The differences in the hygroscopicity of low-substituted methylated celluloses apparently depend in the main upon the internal structure of the cellulose alone. It is not impossible that the hydrophobicity of the radicals introduced affects

the hygroscopicity, the rise in hygroscopicity being slowed down as the number added increases.

The tendency to hydrolyze is a factor that changes more markedly when different numbers of alkyl groups are introduced; it thus made it possible to establish fairly clearly that the degree of polymerization has no effect upon the ease with which cellulose is attacked by a reagent.

Figure 5 reproduces the hydrolyzability of low-methylated cellulose samples of various degrees of polymerization as a function of their percentages of methoxy groups.

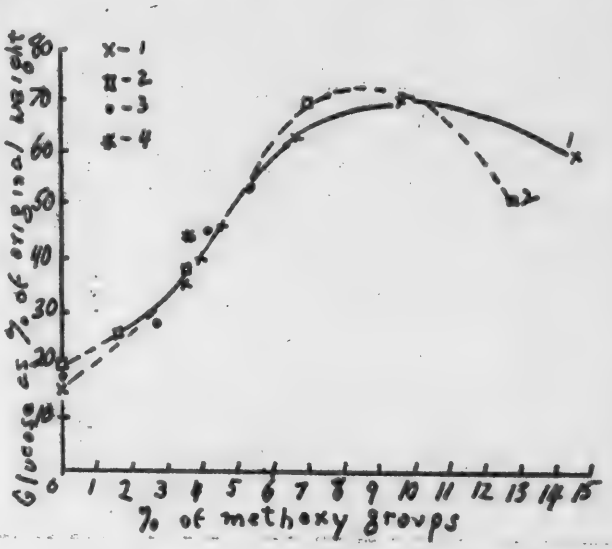


Fig. 5. Hydrolyzability of methylated cellulose

1-Methylation lasting 4 hours at 50 °C, degree of polymerization~400; 2-methylation lasting 22 hours at 50 °C, degree of polymerization~100; 3-Same conditions, methylation in acetone, degree of polymerization~230; 4-same conditions, Hess methylation, degree of polymerization ~800.

Curve 1 represents the hydrolyzability of samples produced by alkylating mercerized cellulose in methyl iodide vapor for 4 hours at 50°C; Curve 2 applies to the same sample and the same experimental conditions, but with the time prolonged to 22 hours. We were unable to secure complete curves for samples produced by other methods, and they are represented in the graph by symbols. An inspection of the diagram is enough to convince one that the hydrolyzability of low-methylated cellulose produced from natural cellulose does not vary with the degree of polymerization. The slight deviation exhibited by Curve 1 cannot be attributed to the degree of polymerization of the samples, being probably related to the fact that these samples underwent considerable destruction during the preparatory process, so that much of them (about 35% in the sample treated with 12.8% OCH_3) dissolved during preparatory washing. In every case we used samples of alkylated cellulose after washing, i.e., after removal of their water-soluble portions, in our determinations of hygroscopicity and hydrolyzability. After such treatment the system had some sort of new internal structure, of course, and could not conserve the same behavior pattern of changes in properties that was observed in samples with higher degrees of polymerization and not so soluble.

The absence of any detectable effect of the size of the cellulose chains upon the hygroscopicity and hydrolyzability of cellulose may also be seen in the samples of mercerized cellulose, some data for which have been published in a previous paper by Nikitin and Klenkova [8]. A comparison of the magnitude of hygroscopicity and hydrolyzability of two samples of cellulose, differing solely in the temperature at which they were treated, is of particular interest. One of the samples was kept at 50° C in a tightly sealed vat for 22 hours after having been mercerized with a 17.5% solution of caustic soda and pressed out to three times its weight; the other received the same treatment for 22 hours at room temperature. After both samples had been washed and dried under identical conditions, their hydrolyzability and water absorption were tested. The results of these tests are

TABLE 6

Properties of Samples of Mercerized Cellulose

Samples tested	Mean degree of polymerization	Per cent moisture absorbed at following percentage relative humidities:					Per cent glucose after boiling for 4 hours with 5% H_2SO_4
		100	87.7	69.8	40.6	6.7	
Cotton lint, mercerized, squeezed out, and kept 22 hours at room temperature...	690	30.3	15.9	10.7	7.5	1.5	13.2
Cotton lint, mercerized, squeezed out, and kept 22 hours at 50° C	96	26.3	15.8	10.4	7.3	1.8	12.9

listed in Table 6.

Notwithstanding the very large difference between the two degrees of polymerization, the hygroscopicity and the hydrolyzability of the tested samples of cotton cellulose, mercerized at different temperatures, were practically identical. Exactly the same results were secured with ramie fibers subjected to the same treatment.

When we consider all these data, we get the impression that the hygroscopicity and hydrolyzability of cellulose systems of similar structure are not affected by changes in the degree of polymerization.

It may be assumed that the hygroscopicity and the hydrolyzability of cellulose systems do not depend, or, in any event, do not noticeably depend, upon the degree of polymerization of the chain molecules, and that the decisive factor is the arrangement of these chains, i.e., the internal structure of the cellulose and its packing density.

Rogovin [11] discussed the problem of the sharp differences in the solubility of viscose rayon fibers of the same degree of polymerization, but produced by different methods of spinning and possessing different structures, and came to the conclusion that the differences in the solubility of preparations having the same degree of polymerization and the same chemical composition are due to differences in the strength of the bonds within the macromolecule. Differences in the structure of the cellulose material, affecting the different packing densities of the macromolecule, may determine the differences in the degree of mutual saturation of the individual polar groups, the formation of different quantities of stronger (hydrogen) bonds, and thus differences in the solubility of preparations of identical degrees of polymerization. Similar considerations apply to the differences in the hygroscopicity and hydrolyzability of cellulose materials.

A study of the physicochemical properties of low-substituted, oxyethylated cellulose has yielded extremely interesting results. Shorygin and Rymashevskaya [12], Nikitin and Rudneva [13], Shorger [14], and other research workers have been treating cellulose with ethylene oxide in recent years. Ethylene oxide is an extremely powerful alkylating agent for cellulose, differing from methyl iodide and ethyl iodide in that it readily forms low-substituted, oxyethylated cellulose systems even at room temperature, which makes it possible to retain a fairly high degree of polymerization. A slightly oxyethylated cellulose was produced in these researches by treating cotton lint, which had been mercerized with a 17.5% solution of caustic soda and squeezed out to 4 times its original weight, with ethylene

oxide vapor at 20° C for 1.5 hours in tightly sealed vats. By using gradually increasing amounts of ethylene oxide they were able to secure a series of oxyethylated fibrous celluloses containing 5.5 to 13.1% of oxyethoxy groups. The resultant samples were washed with dilute acetic acid and water and dried at room temperature. The oxyethoxy groups were determined by the Viebock and Schwappach method [13]. The results of the determinations of the yields of oxyethoxycellulose after the mercerized cotton lint had been treated with ethylene oxide, and the hygroscopicity, hydrolyzability, and degree of polymerization of the end products are listed in Table 7.

TABLE 7

Properties of Oxyethylated Cellulose

Tested material		Yield after treatment, %	Degree of polymerization	Per cent moisture absorbed at relative humidities (%) of:				Per cent glucose after boiling with 5% H_2SO_4	
				1[illegible]	76.6	44.6	11.9	4 hrs.	8 hrs.
Original cotton lint		–	1360	22.6	–	6.0	–	8.2	10.0
Lint, mercerized under oxyethylating conditions (but without ethylene oxide).....		–	960	–	–	–	–	–	19.0
Oxyethylated cotton lint, containing $OCH_2CH_2HO_2H$, %	5.5	101.5	962	24.9	15.9	9.0	4.1	49.1	52.3
	6.1	102.6	–	25.5	16.6	9.5	4.0	–	58.6
	8.7	103.6	900	26.9	17.3	9.5	4.0	58.5	69.4
	10.8	105.6	–	30.5	18.0	9.6	3.9	63.3	70.2
	12.9	106.1	810	31.3	18.1	9.7	3.5	63.2	66.1
	13.1	102.4	–	–	–	–	–	61.8	65.0

Table 7 indicates that introducing an increasing percentage of oxyethoxy groups into cellulose (up to a certain limit) increases the susceptibility of the system to hydrolysis and its hygroscopicity, as was the case with ethoxy and methoxy groups. Comparison of the hydrolyzability of the oxyethoxy samples with that of the ethylated ones indicates that the differences between the hydrolyzability of the samples are very high for identical numbers of groups introduced, despite the approximately equal size of the oxyethoxy groups. On the other hand, when we compare the hydrolyzability of samples of oxyethylated and methylated cotton lint, we see that introducing methoxy groups enables us to achieve the same degree of hydrolyzability as with oxyethoxy groups, notwithstanding the fact that they are smaller than the oxyethoxy groups. Apparently, both the size of the introduced radicals and their nature, i.e., whether they are hydrophobic or hydrophilic, affect the extent of disintegration of the structure. Then the ability to absorb water will be governed, on the one hand, by the general dilation of the system, and on the other by the repellant or attractive action of hydrophobic or hydrophilic groups. The nature of the groups probably affects the susceptibility of the glucoside bonds to hydrolysis as well. Thus, the ethoxy groups result in a lower hydrolyzability than the methoxy groups, in spite of the greater dilation of their structure (as indicated by the hygroscopicity data). This may occur upon either of the two following suppositions: 1) that the methoxy groups themselves offer less opposition to the penetration of the hydrolyzing agent to the glucoside bonds than do the ethoxy groups; or 2) the hydrophobic groups strengthen the glucoside bond in some way or other. Hydrophilic groups, such as the ethoxy compounds,

may, on the contrary, weaken the glucoside bonds in some manner.

In order to explore the effect of the degree of polymerization upon the hydrolyzability of oxyethylated cellulose, in addition to the samples considered above, we prepared a series of slightly oxyethylated celluloses whose degrees of polymerization ranged from 570 to 600, plus two samples with degrees of polymerization of 245-290. To reduce the degree of polymerization below that in the first experiments, the mercerized, squeezed-out cellulose was destroyed at 40-50°C prior to its treatment with ethylene oxide. As before, the ethylene oxide treatment lasted 1.5 hours at 20°C. The results of the determination of the hygroscopicity of the samples, which were washed and dried at room temperature, are given in Table 8.

TABLE 8

Hydrolyzability of Various Samples of Oxyethylated Cellulose

Material tested		Yield after treatment, %	Degree of polymerization	Per cent glucose after boiling with 5% H_2SO_4 for 8 hours
Cotton lint, mercerized, squeezed out, and kept under oxyethylating conditions (but without ethylene oxide).....		–	600	20.4
Oxyethylated cotton lint, containing OCH_2CH_2OH, %	1.6	–	–	26.5
	2.8	–	–	36.1
	3.9	102.4	590	44.3
	6.2	104.1	584	59.7
	8.3	106.0	570	70.3
Oxyethylated cotton lint, containing OCH_2CH_2OH, %	5.8	100.7	290	53.6
	12.4	99.8	245	69.5

The hydrolyzability is plotted as a function of the percent of oxyethoxy groups introduced into the system in Fig. 6. This figure shows that the hydrolyzability for samples of various degrees of polymerization fits a single curve fairly well, and that there can be no doubt that the degree of polymerization has no effect upon the hydrolyzability of slightly oxyethylated natural cellulose.

When we compare the curves for the methylated and oxyethylated celluloses, we are struck by the fact that Curve 2, for the hydrolyzability of slightly methylated cellulose coincides approximately with the curve for slightly oxyethylated cellulose. In both systems, the hydrolyzability maximum lies at 70% of glucose (computed in terms of the absolute dry weight of the sample).

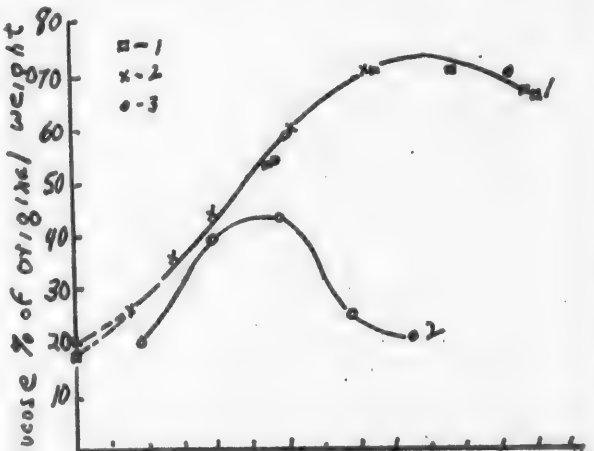


Fig. 6. Hydrolyzability of oxyethylated (1) and methylated (2) cellulose.

Degree of polymerization: 1-900-960, 2-570-600, 3-245-290

The only difference is that to give a system the same susceptibility to hydrolysis, somewhat more methoxy groups must be added than oxyethoxy groups. For example, to secure 50% of glucose under the specified hydrolysis conditions from slightly methylated cellulose, there must be one methoxy group for every 3-4 glucoside residues of the cellulose chain; the same hydrolyzability is achieved with an oxyethylated cellulose by adding one oxyethoxy group per 6 glucoside residues.

SUMMARY

1. Introducing a small number of alkyl (methoxy, ethoxy, or oxyethoxy) groups into a cellulose system ruptures the hydrogen bonds in the transverse structure of the cellulose fiber, resulting in an increase in the hygroscopicity and hydrolyzability of the final systems; this is evidence of a dilation of the internal structure of the fiber. This effect increases with an increase in the extent of substitution (up to a certain limit).

2. The rise in hydrolyzability is especially marked during alkylation. The initial cotton lint yields 10% of reducing sugars in the hydrolyzate after 8 hours of hydrolysis with 5% sulfuric acid (in terms of glucose as per cent of the original weight of the sample), while mercerized lint yields up to 21% glucose with the maximum swelling of the sample, and low-substituted, methylated and oxyethylated samples of the same cellulose material, containing 7-8% of alkyl groups, yield as much as 80% of reducing sugars (in terms of the cellulose portion of the sample).

3. The dilation of the cellulose structure and the manifestation of the properties of hydroscopicity and hydrolyzability when alkyl groups are introduced into the cellulose depend upon the length of the radical introduced as well as upon whether it is hydrophobic or hydrophilic.

4. The degree of polymerization of the chain molecules in cellulose has no detectable effect upon the hygroscopicity or hydrolyzability of cellulose systems.

LITERATURE CITED

[1] P. Hermans. Contribution to the Physics of Cellulose Fibers (1946); P. Hermans, Wermaas, H. Hermans, Kolloid Z., 109, 9 (1944); Nickerson, Ind. Eng. Chem., 1480, 1149 (1942); 34, 85 (1942); 33, 1022 (1941); Nickerson and Habrle, Ind. Eng. Chem., 39, 1507 (1947).

[2] Lorand, Ind. Eng. Chem., 30, 1206 (1938).

[3] Bletzinger, Ind. Eng. Chem., 35, 474 (1943); Aiken, Ind. Eng. Chem., 35, 1206 (1943).

[4] Jayme und Froundjian, Celluloschemie, 18, 9 (1940).

[5] Nikitin, Plekhanova, and Rudneva, J.Appl.Chem. 20, 1185 (1947).

[6] V.Nikitin, J. Phys. Chem., 23, 775 (1949); 23, 786 (1949).

[7] Cited in Demyanov and Pryanishnikov. General Methods of Analysis of Vegetable Substances, 164 (1934).

[8] Nikitin and Klenkova. Researches on High-Molecular Compounds, 137. USSR Acad.Sci.Press (1949).

[9] Tsvetaeva and Nikitin, Trans. Molotov Institute of Technology, Leningrad (1950).

[10] Hess, Trogus, Eveking, Garthe, Ann., 506, 266 (1933).

[11] Rogovin. New Developments in the Chemistry of Cellulose, 30-40 (1945).

[12] Shorygin and Rymashevskaya, Synthetic Fibers, 6, (1933); J. Gen.Chem. 6, 1632 (1936).

[13] Nikitin and Rudneva, J. Appl. Chem. 8, 1023 (1935).

[14] Shorger and Schoemaker, Ind. Eng. Chem., 28, 114 (1937).

Received August 7, 1950.

CHANGES IN THE CHEMICAL AND MECHANICAL PROPERTIES OF CHLORINATED POLYVINYL CHLORIDE AT HIGH TEMPERATURES*

A. A. Berlin and I. I. Denker

The researches of several investigators have demonstrated that when heated, polyvinyl chloride as well as chlorinated rubber [1] undergo dehydrochlorination, resulting in the formation of an insoluble product.

The splitting out of hydrogen chloride is accelerated considerably if the chlorine derivatives of the high-molecular hydrocarbons are subjected to the action of alkalies or bases [2,3].

The present paper deals with the problem of the mechanism involved in the changes of the chemical structure and the mechanical properties of chlorinated polyvinyl chloride (perchlorovinyl) when this polymer is acted upon by high temperatures and basic reagents.

EXPERIMENTAL

When a perchlorovinylic resin is heated from 80 to 130° C, we observe the evolution of HCl and a decrease in the solubility of the product in acetone, chlorobenzene, and other solvents. The pertinent experimental data are listed in Table 1 and plotted in Fig. 1.

The figures in Table 1 indicate that the heat treatment of the product at high temperatures causes a loss in solubility even when insignificant amounts of hydrogen chloride are split out.

Apparently, at a higher temperature the double bonds formed as the result of dehydrochlorination are largely susceptible to intermolecular reaction, resulting in the formation of trimers.

We made a study of the behavior of dilute solutions of perchlorovinyl in pyridine in order to check the correctness of the assumption that an unsaturated high-molecular product capable of polymerization to a trimer is formed during the dehydrochlorination of perchlorovinyl.

This procedure made it possible to slow down the trimer polymerization and to isolate and study the product formed as the result of dehydrochlorination at various stages of the process.

As we see from the figures in Table 2, when perchlorovinyl is heated to 130°C, the time required for the formation of an insoluble polymer increases as the concentration of the pyridine solution of the perchlorovinylic resin is reduced from 10 to 2%. Heating a 2% pyridine solution of the chlorinated polyvinyl chloride to 80°C enabled us to secure a soluble polymer even when the hydrogen chloride evolved totaled 1.7% by weight of the resin (Table 3). The longer the heating time, the greater the extent of dehydrochlorination (Fig. 2). The method we have developed made it possible to establish the existence of a direct relationship

*Report IV of a series on the chemistry and technology of high-molecular compounds.

TABLE 1

Splitting Out of Hydrogen Chloride From a Perchlorovinylic Resin and Change in Its Solubility During Heat Treatment.

Heating temp., °C	Heating time, hours	HCl split out, per cent of resin by wt.	Solubility in chlorobenzene, per cent
80	72	0.07	100
100	24	0.11	100
100	48	0.21	100
100	72	0.661	86.7
130	1	0.04	100
130	2	0.18	80.0
130	3	0.301	63.2
130	8	0.65	0
130	12	0.68	0
130	24	1.75	0

TABLE 2

Gelation Time of Pyridine Solutions of a Perchlorovinylic Resin as a Function of the Concentration.

Concentration of the pyridine solution, %	Heating temperature, hours	Gelation time, minutes
2	130	60
5	130	30
8	130	18
10	130	15

TABLE 3

Splitting Out of Hydrogen Chloride and Change in the Solubility of the Resin During Heating of 2% Solutions of Chlorinated Polyvinyl Chloride

Heating time, hr.	HCl split out, %	Solubility of the resin in chlorobenzene, %
2	0.82	100
4	0.91	100
6	1.70	–

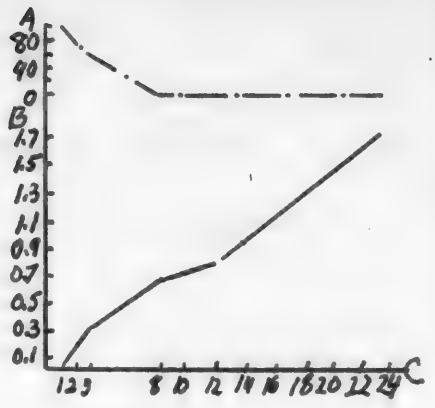


Fig. 1. Variation of the thermal stability of a perchlorovinylic resin with temperature and heating time.

A-Solubility,%; B-HCl split out,%; C-Time, hours.

Scale: 1 mm - 0.02% HCl; 1 mm - 4% solubility; 5 mm - 1 hour.

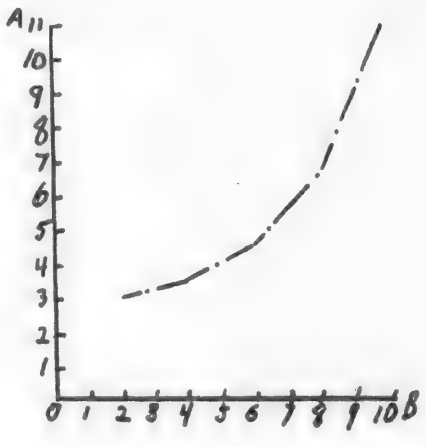


Fig. 2. Iodine numbers as a function of the time the resin is heated in pyridine.

A-Iodine numbers; B-time, hours.

Scale: 1 cm - 1 hr.; 1 cm - 1.0 iodine no.

between the iodine number and the quantity of hydrogen chloride split out.

The pertinent experimental data are given in Table 4.

The possibility of interaction between the macromolecules depends largely upon the temperature and the nature of the medium.

When the resin is heated in the solid phase, i.e., when it is much less possible for the macromolecules to interact, much higher heating temperatures must be employed: 130°C for 25 minutes in our case.

TABLE 4

Change in the Iodine Number of a Perchlorovinylic Resin as a Function of the Length of Time 2% Pyridine Solutions Are Heated to 80°C

Heating time, hr.	HCl split out, %	Iodine number
0	0	0
2	0.82	3.05
4	0.91	3.59
6	1.71	4.60
8	–	7.80
10	–	12.60

TABLE 5

Change in the Solubility of a Perchlorovinylic Resin Containing Double Bonds as a Function of the Heating Temperature

Heating temp., °C	Heating time (minutes)				
	25	50	75	100	125
	Solubility, % of resin by weight				
80	100	100	100	100	100
100	100	100	100	100	100
130	0	0	0	0	0

TABLE 6

Change in the Iodine Number During Heating

Heating time, min.	Heating temp., °C	Solubility of the resin, % of the resin by weight	Iodine number
0	20	100	3.81
25	130	0	4.03
50	130	0	4.08
75	130	0	3.8
100	130	0	4.39

The solubility of this resin (with an iodine number of 3.81) underwent no change when heated for a greater length of time at 100°C (Table 5).

When a relatively concentrated solution of the resin is heated, it is converted into the insoluble state at much lower temperatures. A 5% solution of the perchlorovinylic resin with an iodine number of 3.81 in butyl acetate begins to gel after being kept at 20°C for 24 hours. If the concentration is raised to 15%, the resin loses its solubility even at higher temperatures once it has been exposed to 20°C for 30 hours.

It should be noted that highly concentrated solutions (20%) of a perchlorovinylic resin that do not contain free double bonds are quite stable, undergoing no change when stored for months or even years.

The cited data indicate that the formation of "trimeric structures" of the perchlorovinylic resin, containing free double bonds, takes place at much lower temperatures in solution than is the case in the solid phase. This is due to the much greater mobility of the individual macromolecules (or of their individual links) in the solution, thus increasing the possibility and the probability of intermolecular action between the double bonds.

The conversion of a resin containing free double bonds into the insoluble state ought to involve a diminution in the degree of unsaturation, so that the iodine numbers of the products should, it seems, diminish accordingly. Measurements have shown, however, that when the resin was heated to 130°C, even for 75-100 minutes, so that the solubility of the resin vanished completely, the iodine numbers of the end products were not lowered. The experimental figures thereon are listed in Table 6.

This phenomenon, which is incomprehensible at first glance, is due to the fact that more hydrogen chloride is split out during heating, thus establishing new double bonds. The data on the amount of HCl evolved during supplementary heating of the resin with an iodine number of 3.81 are listed in Table 7.

The values of the iodine numbers that resin preparations must have as the result of the splitting out of various quantities of hydrogen chloride may be calculated approximately. The results of such a calculation are given in Table 8.

TABLE 7

Amount of Hydrogen Chloride Split Out During Supplementary Heating of the Resin

Preparation No.	Heating time, minutes	Heating temp., °C	HCl split out, % of the resin by weight
1	25	130	0.3
2	50	130	0.5
3	75	130	0.6
4	100	130	0.89

TABLE 8

Change in Iodine Number as a Function of the Amount of HCl Split Out

Preparation No.	HCl split out, % of resin by wt.	Iodine No. equivalent of the HCl
1	0.3	1.04
2	0.5	1.73
3	0.6	2.08
4	0.89	3.08

Hence, the overall iodine number of the resin after heating, allowing for the supplementary evolution of hydrogen chloride during the heating, should be as follows: Preparation No. 1: 3.81 + 1.04 = 4.85; Preparation No. 2: 3.81 + 1.73 = 5.54; Preparation No. 3: 3.81 + 2.08 = 5.89; Preparation No. 4: 3.81 + 3.08 = 6.89.

When we compare these computed iodine numbers with the numbers experimentally measured in the preparations of perchlorovinylic resin after heating, the regular diminution of the overall values of the preparations' iodine numbers is fairly clear. The pertinent experimental data are listed in Table 9.

TABLE 9

Diminution in the Overall Values of the Iodine Numbers of the Preparations

Preparation No.	Overall iodine numbers	Heating time, minutes	Heating temp., °C	Iodine number after resin has been heated	Diminution of iodine number after heating
1	4.85	25	130	4.03	0.82
2	5.54	50	130	4.08	1.46
3	5.59	75	130	3.80	2.09
4	6.89	100	130	4.39	2.50

The figures listed in this table support our assumption concerning interaction between macromolecules, resulting in a diminution of the number of double bonds.

Effect of heating upon the change in the physical and mechanical properties of perchlorovinyl films. The formation of "trimeric structures" not only results in a decrease in the solubility of the resin, but also in a change in many physical and mechanical properties of the films made thereof.

We investigated this problem by heating films made of perchlorovinylic resin to 130°C for varying periods of time, and then determining their physical and mechanical properties.

Our results are listed in Table 10 and shown in Fig. 3. The data in Table 10 and Fig. 3 show that prolonging the heating of the films to 130°C causes several fundamental changes in their properties. These changes are mainly as follows: 1) the solubility of the films gradually decreases; 2) the tensile strength of the films rises; 3) their elongation drops; and 4) the number of double bends that the films can stand drops considerably.

All these changes are fairly characteristic and they provide further confirmation of the formation of trimeric structures when a perchlorovinylic resin is heated to high temperatures.

TABLE 10

Change in the Physical and Mechanical Properties of Perchlorovinyl Films as the Result of Heating to 130°C

Heating time, hours	Mechanical properties of the films			Solubility of the films in acetone %
	Tensile strength, kg/mm²	Elongation, %	Number of double bends	
0	3.8	5.4	173.0	100
1	4.2	4.2	61.2	78.3
3	4.5	3.0	39.2	60.8
5	4.7	3.0	28.0	0.0
8	5.6	3.4	10.6	0.0

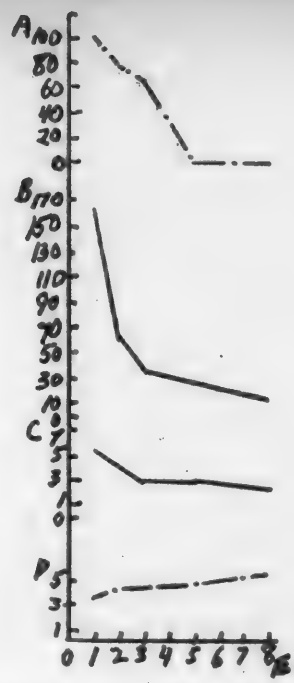


Fig. 3. Change in the physical and mechanical properties of perchlorovinyl films as the result of heating.

A-Solubility,%; B-number of double bends; C-elongation,%; D-tensile strength, kg/mm²; E-time, hours. Temp. - 130 °C. Scale: 5 mm - 1 kg/mm² 5 mm - 1% elongation; 5 mm - 10 double bends; 1 cm - 20% solubility.

SUMMARY

1. The dehydrochlorination of a perchlorovinylic resin at high temperatures results, in its first stage, in the formation of a soluble product containing double bonds.

2. It has been shown that the conversion of chlorinated polyvinyl chloride into an insoluble state as the result of heat treatment is due to the trimeric polymerization of the macromolecules that contain double bonds.

3. It has been found that the trimeric polymerization of an unsaturated perchlorovinylic resin takes place most readily in solutions. Higher temperatures are required to carry out this reaction in the solid phase.

4. It has been established that heat treatment of the films at 135°C increases their tensile strength and diminishes their elongation and flexibility, owing to dehydrochlorination and trimeric polymerization.

LITERATURE CITED

[1] Hoekerra, Kautschuk, 6, 102-112, 7, 137-140 (1939).

[2] Korshak and Zamatina, J.Appl.Chem. 14, 6, 809-816 (1941).

[3] Staudinger, Brunner, Feisst, Helv. Chim. Acta., 13, 805-832 (1930).

Received May 15, 1950.

USING THE METHOD OF DISPERSION IN ANTHRACENE OIL TO CHARACTERIZE THE PROPERTIES OF MINE AND HEATED COAL

V. N. Novikov

Coking coal becomes plastic in the 300-450° temperature range. Coals that do not have this property do not yield fused coke. The interaction of the constituents of the solid, liquid, and gaseous phases, whose proportions vary as the temperature is raised, gives rise to the coking end products as in the form of coke of some definite quality, plus chemical products.

The phenomena that take place thereby have been interpreted differently, and many new ideas have arisen during the last ten to fifteen years in our scientific concepts of the chemical structure of coal and of the processes involved in its pyrogenic treatment.

In recent years the concept of coal as a system of high-molecular compounds of a colloid character has received more and more support. The plastic state of coal and the formation of a coking residue are regarded in the light of physical and chemical processes, as well as of colloid-chemical phenomena. The interpretations of the processes occurring during the stage when the coal is plastic that we are familiar with are based principally upon observations made during studies of the coal in its initial, unheated state. Interpretations of this sort requires, of course, checking and refinement from various points of view.

Observations on the swelling of coal in organic solvents, as well as the formation of colloidal solutions when coal is treated with fractions of the primary tar, anthracene oil, and other solvents that are products of the distillation of coal, lead us to assume that colloid-chemical processes also take place when coking coal enters the plastic state. As we see it, the liquid phase formed as the result of heating and the decomposition of the coal is a dispersion medium, the action of which causes the dispersion of the remaining portions of the coal in one way or another.

The degree of dispersion and the degree of homogeneity of the plastic colloidal system formed as the result of heating may be quite different, depending upon the properties of the original coal. The principal factors governing the formation of the plastic mass are: the thermal stability of the substance in the coal and in the liquid phase that is formed; the quantity and viscosity of the liquid phase; and the quantity of the solid residue that can be peptized and converted into a dispersed state.

Dispersion is accompanied, however, by the pyrogenic decomposition of the constituents of the dispersion medium and the dispersed phase, accompanied by the evolution of a gas phase, the magnitude of which rises sharply during the second stage of plasticity, i.e., above 390-400°. Complicated molecules, the nuclei of which consist of condensed benzene rings, are formed by the splitting off of side chains and other less stable groups and by the condensed polymerization of the decomposition residues.

The subsequent solidifying of the plastic mass is, as may be imagined, related to condensations caused by a change in the properties of the dispersion medium and the dispersed phase as the result of the chemical reactions that occur during the decomposition of the substances participating in the process. The extent of the thermal stability of the components of the liquid and solid phases is the decisive factor in the condensation process.

The formation of condensed molecules leads to an enrichment of the dispersion medium with more high-molecular substances and to a decrease in the degree of dispersion of the dispersed phase. As decomposition progresses, more and more of the condensed molecules are formed, both by the formation of new ones and by the growth of the complexes formed originally.

In ordinary colloidal solutions the first stage of coagulation is the formation of centers of condensation (seeds) as the result of the aggregation of particles and the structuralization of the system. In polydispersed systems the large particles act as condensation centers, the small particles settling on them at a faster rate than on particles of their own size.

During the plastic stage the substance of the coal is a multicomponent, polydispersed system. In such a case, the condensed molecules that already possess a regular chain structure and particles with a low degree of dispersion may act as centers of condensation, and, moreover, condensation may also take place at the surface of nondispersed particles.

This process results in lowering the degree of dispersion of the system and forming of an irreversible residue, which constitutes one of the structures of a semicoke, being distributed as it is among the nondispersed particles of the coal mass, whose properties and structure have also changed in the direction of greater order.

The nature of the processes that take place during the condensation of the plastic mass are of fundamental importance, since it is during this period that the structural features of the coke substance originate, their development and final shaping occurring as the temperature is raised still higher. The ratio between the dispersion medium and the dispersed phase, the degree of dispersion of the coal substance, the rate at which condensation centers arise, and the rate of growth of the aggregates are all essential for the process of condensation of the plastic mass. Various combinations of these factors thus affect the rate of condensation and the rate at which aggregates grow in the resulting residue. When the rate at which centers of condensation are formed is high, while the rate of growth of the aggregates is low, the system is enriched with small aggregates. On the other hand, when the rate at which centers of condensation are formed is low and their rate of growth is high, we get coarse systems that are not very rich in particles.

The viscosity of a colloidal system either promotes or impedes the growth of aggregates. Low viscosity promotes the growth of aggregates by facilitating the motion of particles throughout the system. An increase in viscosity tends to reduce the dimensions of the particles.

The semicoke produced by heating possesses a regular structure, consisting of lattices of condensed nuclei arranged in a definite order. Examinations of the Debye crystallograms of heated coal (the research of Railey and others) has made it possible to determine the principal dimensions of this space lattice.

The views set forth above do not claim, of course, to be a completed theory of the plastic state of coking coals, covering all the diversified phenomena involved. What we are aiming at is an endeavor to provide a new interpretation of

the processes taking place during the softening of coal and the formation of the plastic mass.

This paper reports the results of research conducted at the Eastern Institute of Coal Chemistry to shed some light on some of the problems touched on above.

EXPERIMENTAL

Operational procedure. The research method employed involved the dispersion of coal in anthracene oil at relatively high temperatures (300-350° and up).

We employed this method for the following reasons. In the treatment of coal at temperatures lying at the start of softening and higher, a heavy solvent, in this case anthracene oil, reacts with the decomposition products of the primary structure of the coal to form a colloidal solution. Hence, the magnitude of the dispersed part of the coal may indicate the extent to which the organic mass of the coal can be converted to the dispersed state at the given temperature.

Each new sample of the coal (20 g) was heated to the given temperature, starting with temperatures close to those at which the coal commences to decompose, and ending with the temperature at which the plastic mass solidifies. The coal was heated in a Pyrex glass apparatus [1] as follows: at a rate of 10° per minute until decomposition started (approx. 290°), and at 2.5° per minute thereafter. The sample was kept at the given end temperature for 15 minutes.

The amount of gas, oily distillates, and water, which constitute the gas phase at the temperature of the experiment, was measured accordingly.

The heated coal was pulverized as soon as heating was over, if this was necessary, and divided into two parts. One part was treated with anthracene oil

TABLE 1

Name of coal Kuznetsk Basin	Grade	Proximate analysis, %			Plastometric parameters, mm	
		Moisture	Ash, in dry coal	Volatiles, in combustible mass	x	y
Leninsk, "Zhurnik" mine	D	7.12	5.01	42.10	45	0
Leninsk, Yaroslavsky mine	G	2.14	9.84	41.35	33	15
Osiniki, Yelbansky seam	PZh	1.81	9.34	27.8	16	32
Prokopyevsk, Voroshilov mine 5/6 ..	KZh	0.90	8.90	23.8	27	16
Anzhero, Mine 9/15..	PS	1.00	8.21	14.5	21	0
Karaganda New Seam..	K	1.59	10.57	30.8	—	—
Kiselevsk, Mine 6, seam 13	-	1.10	18.55	43.9	59	11

by the method described by Zabavin [2]. The solvent used was the fraction of anthracene oil that distils at 350-380°. The dispersion temperature was 350°. The coal was ground to a fineness that passed through a 900 screen (900 openings per cm^2). The sample of coal weighed 2 g, the oil totaled 100 cm^3, and dispersion lasted 4 hours. The amount of coal dispersed was determined from the amount of the undispersed residue. Samples of coal coming from the Yaroslavsky mine in

TABLE 2

Heating temp., °C	Per cent yield: Tar	Pyrogenic water	Gas	Total gas phase (tar, water, gas), %	Dispersed in anthracene oil, % of original coal: Total	Per cent dissolved in alcoholic benzene	Insoluble solid residue, %	Dispersed in anthracene oil, % of non-volatile residue: Total	Per cent dissolved in alcoholic benzene
1	2	3	4	5	6	7	8	9	10
Leninsk coal, "Zhurnik" mine									
Initial	–	–	–	–	74.2	2.78	25.8	–	–
290	0.35	1.18	0.35	1.88	–	4.70	–	–	4.8
310	0.47	1.53	0.45	2.45	–	4.42	–	–	4.5
330	0.68	1.36	0.41	2.45	–	4.47	–	–	4.6
350	1.11	1.21	0.58	2.90	63.1	4.72	34.00	65.0	4.8
370	1.53	2.09	0.78	4.40	63.1	–	32.50	66.0	–
390	2.95	2.78	1.67	7.40	58.1	5.67	34.50	62.7	6.1
410	2.97	2.83	5.15	10.95	38.7	4.02	50.35	43.5	4.5
430	9.35	5.25	5.94	20.54	11.1	2.05	68.36	13.9	2.5
450	13.53	5.56	6.62	25.71	1.1	0.47	73.19	1.4	0.6
Leninsk coal, Yaroslavsky mine									
Initial	–	–	–	–	93.4	1.17	6.6	–	–
290	none	–	0.23	0.23	*	6.36	–	–	–
310	0.11	–	0.35	0.46	76.60	8.26	22.94	76.96	8.30
350	1.69	0.34	0.44	2.47	86.15	9.86	11.38	87.25	10.12
370	2.05	0.72	0.48	3.25	86.60	12.83	10.15	89.90	13.25
390	3.80	0.77	0.75	5.32	84.25	13.81	10.43	89.00	14.60
410	5.60	1.38	1.31	8.29	78.60	14.62	13.11	85.70	15.93
430	11.81	1.83	3.04	16.68	40.05	4.13	43.27	48.0	4.13
450	14.40	2.70	3.68	20.78	12.10	0.72	67.12	15.25	0.91
470	14.83	2.70	4.13	21.66	0.58	0.58	77.76	0.75	0.75
Osiniki coal, Mine 10, Yelbansky seam									
Initial	–	–	–	–	94.25	0.91	5.75	–	–
290	0.05	–	0.18	0.23	–	2.47	–	–	2.5
310	0.30	–	0.22	0.52	–	6.41	–	–	6.5
330	0.52	–	0.24	0.76	–	8.88	–	–	9.0
350	1.01	–	0.61	1.62	91.55	10.30	6.83	92.1	10.5
370	1.66	–	0.67	2.33	89.90	14.22	7.77	92.0	14.6
390	2.01	–	0.73	2.74	89.90	14.95	7.36	92.4	15.4
410	3.64	0.21	2.10	5.84	85.90	15.05	8.26	91.2	16.0
430	7.29	0.85	3.54	11.68	77.40	11.95	10.92	87.5	13.5
450	9.96	0.95	4.11	14.62	31.80	4.04	53.58	37.2	4.7
470	10.11	1.05	4.34	15.50	1.16	1.16	83.34	1.4	1.4

(Table 2 is continued on page 349)

Leninsk, which were heated to 290-310°, were treated with oil at that same temperature. We found that at these temperatures highly viscous, nonfiltering solutions were formed. Complete dispersion took place only at 350°, and all subsequent determinations were made at that temperature.

*Did not disperse.

TABLE 2 (continued)

Heating temp., °C	Per cent yield: Tar	Pyrogenic water	Gas	Total gas phase (tar, water, gas), %	Dispersed in anthracene oil, % of original coal: Total	Per cent dissolved in alcoholic benzene	Insoluble residue, %	Dispersed in anthracene oil, % of non-volatile residue: Total	Per cent dissolved in alcoholic benzene
1	2	3	4	5	6	7	8	9	10
Prokopyevsk, Voroshilov mine 5/6									
Initial	–	–	–	–	79.5	1.73	20.5	–	–
290	0.46	–	0.04	0.50	–	1.94	–	–	2.0
350	1.11	–	0.09	1.20	75.00	6.58	23.80	75.1	6.7
390	1.72	0.13	0.65	2.50	73.10	9.49	24.40	74.9	9.7
410	2.61	0.36	0.78	3.85	68.00	7.36	28.15	70.0	7.7
430	3.53	0.55	1.77	5.85	58.2	5.55	35.95	61.8	5.9
450	5.86	0.69	3.35	9.90	38.1	2.26	52.00	42.2	2.5
470	7.61	1.09	4.30	13.00	8.3	1.52	78.70	9.60	1.7
490	8.93	1.19	6.58	16.70	1.13	1.13	82.17	1.3	1.3
Anzhero, Mine 9/15									
Initial	–	–	–	–	47.2	0.61	52.8	–	–
280	0.26	–	0.24	0.50	–	0.56	–	–	0.56
300	0.46	–	0.14	0.60	–	0.62	–	–	0.62
320	0.61	–	0.24	0.85	–	0.73	–	–	0.74
340	0.65	–	0.35	1.00	–	0.71	–	–	0.72
360	0.65	0.11	0.36	1.12	47.4	0.65	51.48	47.9	0.66
400	0.65	0.37	0.28	1.30	44.0	0.49	54.70	44.0	0.50
420	0.74	0.58	0.26	1.60	41.0	0.44	57.40	41.6	0.45
440	1.08	0.58	0.79	2.45	40.5	0.41	57.05	41.5	0.42
460	1.34	0.84	1.57	3.75	27.0	0.41	69.25	28.0	0.42
480	1.92	0.93	1.70	4.55	15.4	0.41	80.05	16.1	0.43
500	2.20	0.94	2.61	5.75	8.7	–	85.55	9.2	–
520	2.58	1.08	2.82	6.48	0.5	–	93.02	0.5	–
Karaganda Coal, Mine 2, New Seam									
Initial	–	–	–	–	–	1.86	–	–	–
290	0.69	0.12	0.22	1.03	–	2.58	–	–	2.6
310	0.86	0.23	0.25	1.44	–	6.45	–	–	6.5
350	1.34	0.27	0.28	1.89	70.35	7.26	27.76	71.8	7.4
390	1.87	0.29	0.33	2.49	68.85	8.27	28.66	70.7	8.5
410	2.96	0.37	0.44	3.77	–	10.05	–	–	10.5
430	3.02	0.50	0.67	4.19	68.50	10.36	27.31	71.5	10.8
450	4.10	0.94	1.19	6.23	65.60	9.25	28.17	70.0	9.8
470	7.30	1.59	1.77	10.65	47.75	4.18	41.59	53.4	4.7
490	10.49	1.98	5.58	18.05	1.66	1.66	80.29	2.0	2.0
Kiselevsk, Mine 6, seam 13									
Initial	–	–	–	–	70.6	4.23	29.4	–	–
290	1.23	–	0.0	1.23	–	10.1	–	–	10.2
350	2.05	0.06	0.34	2.45	64.70	16.63	32.85	67.70	17.4
390	4.10	0.13	0.87	5.10	76.70	21.23	18.20	80.8	22.4
410	14.15	0.82	3.33	18.30	25.35	15.80	56.35	31.0	19.3
430	20.20	0.89	3.41	24.50	–	–	–		–
450	21.57	0.94	5.69	28.20	7.45	3.26	64.35	10.4	4.5
470	22.68	3.22	6.20	32.10	3.30	1.28	64.60	4.8	1.9

The second portion of the heated coal was extracted with alcoholic benzene to determine the low-fusible substances comprised in the overall extract secured with the anthracene oil. This determination serves as a supplementary index of the percentage of the coal dispersed in the anthracene oil.

Measuring the size of the gas phase entailed no difficulties. The nondispersed residue may be recovered from the nonvolatile residue that participates in the formation of the coke as an inert portion distributed among the "fusible" portion. Lastly, the portion dispersed in the anthracene oil includes elements that impart mobility to the plastic mass, viz.: the liquid phase and the dispersed particles. A method of separating the dispersed particles into the liquid and solid phases has not been worked out as yet, but still this overall determination makes it possible to detect the presence of colloidal properties in heated coal.

The research covered the following coals: Kuznetsk, of varying degrees of metamorphism, ranging from long-flame to poorly coking coal; Karaganda; and Kizelevsk, their names and analyses being given in Table 1.

Our results are compared in Table 2, the yields being given in terms of the combustible material in the coal, and in terms of the organic mass for the Kizelevsk coal.

Fig. 1 shows the rise in the output of tar, water, and gas as the temperature is raised.

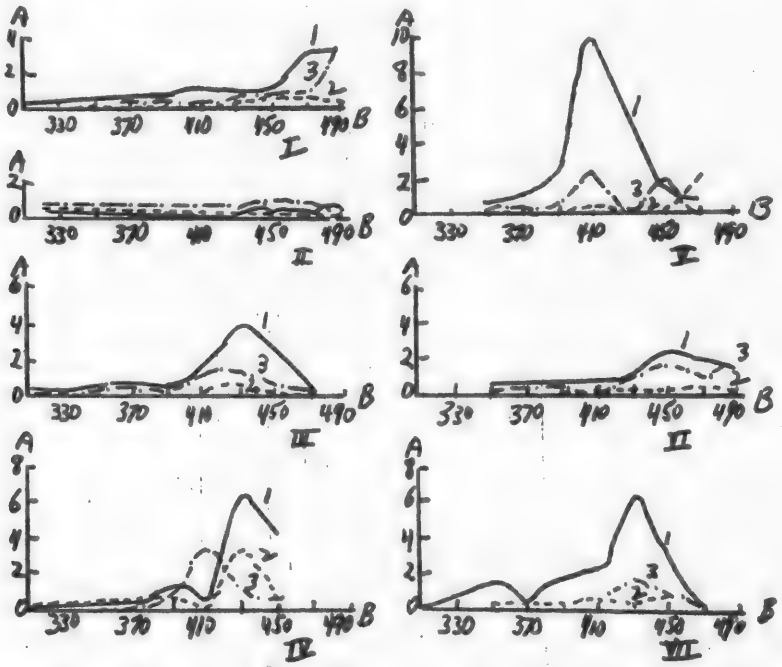


Fig. 1. Variation of the outputs of tar, water, and gas with temperature.

A-% yield; B-temp. °C. 1-Tar; 2-pyrogenic water; 3-gas. Coals: I-Karaganda; II-Anzhero; III-Osiniki; IV-Zhurnik; V-Kizelevsk; VI-Prokopyevsk; VII-Yaroslavsky mine.

Low-melting substances. The substances leached out of the original coal by alcoholic benzene before heating are called "bitumens properly speaking" in the present paper. We consider it proper to retain the term "bitumen" in this case, inasmuch as the extracted substances apparently are actually the residues of natural hydrocarbons. The recovery of oil at low temperatures is often encountered in the analysis of coal.

The substances extracted from the heated coal by alcoholic benzene are called "low-melting substances," since they are not present in ready form in the coal, as we see it, but are formed as the result of the disintegration of the coal by heat.

We can see that there is no relationship between the amount of bitumen extracted by the alcoholic benzene from the initial coal and the amount of low-melting substances formed during heating. The changes in the amount of low-melting substances are quite definitely related, however, to the general nature of the organic material in the coal and to its coking properties. In good coking coals the quantity of low-melting substances rises sharply at low temperatures, when no decomposition of the coal with any detectable evolution of gaseous products occurs as yet (Table 3).

TABLE 3

Name of coal	Per cent yield of alcoholic benzene extract				
	Initial coal	Coal heated to 290°		Coal heated to optimum temperature	
		Output	% increase	Output	% increase
Leninsk, "Zhurnik" mine ...	2.78	4.70	169	5.67	204
Leninsk, Yaroslavsky mine..	1.17	6.36	543	14.62	1249
Osiniki	0.91	2.47	272	15.05	1654
Prokopyevsk	1.73	1.94	112	9.49	548
Anzhero	0.61	0.59	96	0.73	120
Karaganda	1.86	2.58	139	10.36	557
Kizelevsk	4.23	10.1	234	21.23	502

The quantity of low-melting substances attains a maximum at temperatures that are either the same as the temperatures of maximum dispersion or are close to them. Coals with poorer coking properties (Prokopyevsk or Karaganda coal) yield less low-melting substances at low temperatures or at the temperature corresponding to their maximum yields.*

This is not true of noncoking coals. Zhurnik (D) coal, for instance, yields an extremely small output of low-melting substances when heated, notwithstanding the fact that it is on a par with Karaganda coal as far as its dispersibility in anthracene oil is concerned. It is characteristic that the quantity of low-melting substances, though it increases somewhat at 290°, exhibits practically no change as the temperature is raised still higher. The same is true of Anzhero coal: The quantity of low-melting substances is extremely low and exhibits hardly any change upon heating.

The quantity of substances leached out with alcoholic benzene may serve as one of the indirect indexes of the viscosity of the liquid portion formed during the heating of the coal, at the same time indicating the viscosity of the plastic mass.** The higher the proportion of low-melting components in the general dispersed portion, the lower should be the viscosity of the plastic mass, all other conditions remaining the same.

The low-melting substances are given in Table 4 as percentages of the portion of the coal dispersed in the anthracene oil during the period corresponding to the maximum formation of low melting substances.

*The rise in the alcoholic-benzene extract when the coal is heated is also reported in papers by Gorftman, Kopelevich and Kagan [3,4] and Anurov and Obukhovsky [5].

**Moreover, the viscosity of the liquid portion depends upon the molecular weight and the structure of the substances comprising it; it may change considerably, depending upon the carbon content of the coal.

According to these figures, the minimum viscosity should be manifested by the fusible portion of Kizelevsk coal, the low-melting substances of which total nearly 28%.

In the genetic series of Kuznetsk coals, the dispersed portion of Leninsk coal ought to have the lowest viscosity; it is followed by Osiniki and Prokopyevsk coal, with the Anzhero coal bringing up the end of the parade. In this series, Karaganda coal lies between the Osiniki and Prokopyevsk coals.

TABLE 4

Name of coal	% low-melting substances
Zhurnik mine.	9.7
Leninsk	18.6
Osiniki	17.5
Prokopyevsk..	12.9
Anzhero	1.52
Karaganda ...	15.1
Kizelevsk ...	27.7

Results of dispersion in anthracene oil. In nearly every case, heating the coal results in some diminution of its dispersibility in anthracene oil. Anzhero coal, in which the dispersed portion increases somewhat, and Kizelevsk coal are exceptions to this rule.

We see that heating the coal affects the ability of the coal to disperse in anthracene oil variously. This is true for both the total amount dispersed and for the temperature range in which the ability of the coal to enter the dispersed state is exhibited (Table 5).

Osiniki fat coking coal has the highest degree of dispersion during heating. Coals that have a higher or lower carbon content also have a smaller dispersed fraction.

TABLE 5

Name of coal	Maximum dispersibility	
	Temperature range, °C	Yield, in % of the nonvolatile residue
Leninsk, Zhurnik mine.....	350-370	65.0-66.0
Leninsk, Yaroslavsky mine...	370-390	89.9-89.0
Osiniki.....	350-390	92.1-91.2
Prokopyevsk.....	350-390	75.1-74.9
Anzhero.....	360	47.9
Karaganda.....	350-450	71.8-70.0
Kizelevsk.....	390	80.8

The temperatures at which dispersibility is a maximum are lowest for the end members of the homologous series: 350-370° for Zhurnik coal, and 360° for Anzhero coal, whereas the high output of the dispersed fraction is maintained fairly constant through a wider temperature range, up to high temperatures of the order of 390°, for Leninsk, Osiniki, and Propkopyevsk soals. Karaganda coal is remarkable in that its yield of the dispersed fraction remains constant throughout the range of 350-450°.

Decomposition of the coal and condensation of the plastic mass. When we inspect the experimental data (Table 2 and Figure 2, in which there are plotted the curves that indicate the quantity of the fraction dispersed in anthracene oil as the temperature to which the coal is heated is raised), we see appreciable differences in the behavior of the different coals during the condensation of the plastic mass.

Leninsk coal from the Yaroslavsky mine possesses high fusibility. The nonvolatile residue capable of dispersion totals some 90%, 14-16% of it being low-melting substances. This is evidence of the comparatively homogeneous nature of the plastic mass in this coal. When observed under the microscope, Leninsk coking coal is completely transformed into a liquid mass upon heating, in which no traces of any solid particles can be detected. All of this liquid mass changes from a mobile state to a stage of boiling and gradually solidifies.

The following factors affect the nature of condensation of the Leninsk coal

plastic mass. The nondispersed fraction is small. The viscosity of the liquid phase is low, compared to that of the other coals, as is indicated by the high percentage of low-melting substances in the dispersed fraction (Table 4). The

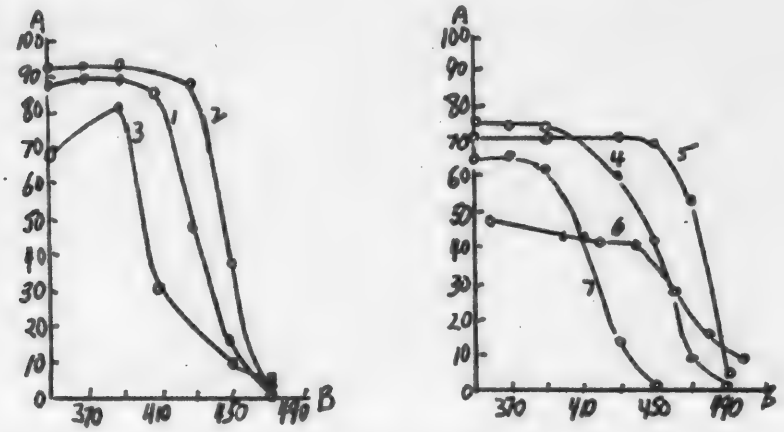


Fig. 2. Variation with temperature of the quantity of nonvolatile residue dispersible in anthracene oil.

A-% of dispersd nonvolatile residue; B-temp. °C.
Coals: 1-Yaroslavsky mine; 2-Osiniki; 3-Kizelevsk; 4-Mine 5/6; 5-Karaganda; 6-Anzhero; 7-Zhurnik mine.

period during which maximum dispersibility of the nonvolatile residue is maintained is brief. Condensation takes place very rapidly. The amount of tar rises gradually at first, with a sharp increase taking place at 430°. There is not much pyrogenic water, and no marked changes can be observed in its formation.

The quantity of gas evolved rises sharply at 430°. The gas phase increases considerably in the 410-430° interval, owing to a marked change in the decomposition of the coal. The gas phase totals 20.78% at 450°. The fact that decomposition is greatest (8.57% between 450 and 470°) toward the end of condensation is an adverse factor. The evolved gases largely break up the growing structure of the semicoke.

Osiniki coal (Zh) possesses the highest capacity for entering the dispersed state of all the coals tested. When it is heated, 92.4% of the nonvolatile residue is dispersed in the anthracene oil, up to 16% of this total consisting of low-melting substances. The nondispersed residue totals only 6.83%.

The fact that the number of nondispersed particles is small at the beginning of condensation, which evidences the homogeneity of the plastic mass, affects the nature of the condenaation of the Osiniki coal's plastic mass.

The condensation interval is even briefer than is the case of the Leninsk coal. There are also differences, however, in the course of the condensation and in the parallel process of decomposition. Less of a gas phase is evolved during the decomposition of the organic material of Osiniki coal in the same temperature range as used for the Leninsk coal. Though some tar and gas are evolved below 410°, their quantities are negligible. The temperature of 410° is the level at which the rate of course of the processes change markedly. After a marked reduction in dispersibility and the onset of the decomposition of the low-melting substances, the outputs of tar, gas, and pyrogenic water gradually begin to increase, though the aggregate output is less than that of the Leninsk coal. These symptoms, together with the narrow condensation interval and the temperature at which

decomposition sets in (which is higher than that for the Leninsk coal), are evidence of greater homogeneity and denser structure of the molecules of the organic material, which are among the reasons for the high viscosity of the plastic mass of Osiniki fat coking coal.

Prokopyevsk coal from the Voroshilov mine (KZh) exhibits a much smaller tendency to enter the dispersed state. The percentage represented by the dispersed fraction of the nonvolatile residue after heating is only 75%, 9.7% of which represents low-melting substances. The plastic mass of this coal, which has a higher degree of metamorphism than the Osiniki coal coming from the Yelbansk mine, exhibits considerable heterogeneity. The liquid portion of the plastic mass, formed from the even more highly condensed molecules, with a small percentage of low-melting fractions (Table 4), must display even higher viscosity. In this instance, the swelling of the plastic mass is prevented by the presence of the infusible fractions, which give the system its heterogeneity.

The condensation curve exhibits no sharp discontinuities. The condensation period is longer than that of the Leninsk and Osiniki coals and, hence, condensation is slower.

The gas phase formed during the period of condensation is even smaller than in the Osiniki coal, resulting in the formation of a stronger structure.

In the Anzhero coal, which stands highest in the genetic series of the tested Kuzetsk coals as far as metamorphism is concerned, the colloid-chemical properties are least evident – only 48% is dispersed in the anthracene oil, the low-melting substances constituting only 0.74% and the percentage of undispersed particles never falling below 51%. The period of condensation is extremely prolonged for Anzhero coal. In this case, the insufficiency of the dispersed fraction and the high viscosity of the liquid fraction, which does not facilitate the formation of well-fused coke, greatly affect the strength of the coke. The volume of the gas phase formed during the decomposition of Anzhero coal is small, so that this factor is unimportant.

"Zhurnik" coal, which has no coking properties, despite the fact that up to 69% of the nonvolatile residue dispersed in anthracene oil, is of particular interest. Hence, much of the organic material in "Zhurnik" coal can enter the dispersed state during heating, if the conditions are right.

When "Zhurnik" coal is heated, much more pyrogenic water is formed than in the case of the other coals, even at low temperatures. The percentage of low-melting substances soluble in alcoholic benzene is low. Their output changes extremely little (4.7 – 5.6 – 4.0%) in the temperature range from 290 to 410°. A sharp drop is observed only at 430°.

The outputs of tar, gas, and water increase up to 390°, though slowly. The output of gas begins to rise, and the outputs of tar and water rise sharply at 430°. This leads us to believe that in the heating of "Zhurnik" coal, the liquid phase (at the temperature to which the coal is heated) is not large and that, what is most important, it is rapidly decomposed, since it is enriched with unstable oxygen compounds.

In contrast to the coal from the Yaroslavsky mine, most of the tar is formed at high temperatures, which is not related to the quantity of low-melting substances. Here the solid phase of the coal is decomposed at once into compounds that are unstable at the prevailing temperature, without going through the stage in which a stable liquid phase is formed, as is the case with the coking coals; this must be due to the weakness of the molecular structure as the result of weak oxygen bonds.

That is why the solid phase is not dispersed, the coal does not become

plastic, and no fused coke is formed.

In Karaganda coal about 30% of the nonvolatile residue is not dispersed, and, hence, its plastic mass is heterogeneous. In this respect Karaganda coal resembles the coal from the 5/6 Mine of the Kuznetsk Basin. The percentage of low-melting substances rises gradually, attaining 10.4% at 430°, but dropping rapidly as the temperature is raised still higher. In contrast to the Kuznetsk coals, more tar, gas, and water is formed from the Karanganda coal at low temperatures. The decomposition of the coal is accelerated at 450°, which entails the beginning of a drop in dispersibility. Karaganda coal exhibits a high rate of condensation, of the same order of magnitude as Osiniki coal. To judge from the percentage of low-melting substances, the viscosity of the dispersed fraction is much the same as that of the Osiniki coal.

Kizelevsk coal differs from the other coals tested in its high percentage of bitumens properly speaking (4.23%) and in its high yield of low-melting substances at low temperatures. The dispersed fraction of the nonvolatile residue totals 81%, of which 22.4% constitutes low-melting substances.

The primary tar, which is produced in abundance, condenses with the cold portions of the charge and increases the volume of the liquid phase even more. But alongside this large volume of the liquid phase, which is not encountered in the other coals, however, the dispersibility of the coal is not as high, under the given experimental conditions, as might have been expected from our observations of the way in which the coal fused during heating. The "leaking" of Kizelevsk coals from the Sapozhnikov plastometric apparatus is a well-known fact that testifies to the high fusibility of the coal and the mobility of its plastic mass.

The maximum dispersion, 80.8%, is noted at 390°, after which the dispersed fraction diminishes rapidly. Intensive decomposition likewise sets in at 390°. The output of tar, water, and gas goes up with a jump after the dispersibility drops off and the output of low-melting substances diminishes. Kizelevsk coal is a sporal durain containing as much as 40% of spores (not recomputed on the basis of the organic material). Obviously, the residues of regular elements are also responsible for the low dispersibility of Kizelevsk coal.

Under the microscope the first thing we observed was the liquid mass leaking out of the grains of coal, which gradually fused. But at the same time we noticed that the residue resembled the previous forms, and we saw that some of the coal did not melt. Some sort of stable system was preserved even in the ensuing heating stage, when the melted mass entered a stage that resembled boiling.

The plastic mass does not condense at a uniform rate: condensation is extremely rapid at first (390-410°), slowing down in the 410-480° interval, with an abundance of gas evolved in the latter period.

Thus, the determination of the changes in the dispersibility of coal when heated, together with a determination of the percentage of gaseous products evolved, employed as a method of research, provides a clearer notion of the course of condensation of the plastic mass and of the properties of the resultant coke.

SUMMARY

1. In the present research, bituminous coal is considered to be a colloid-chemical system within the temperature range at which it is plastic, formed as the result of thermal decomposition and constantly changing its properties as the temperature is raised. The method employed to identify the colloidal properties of this system was the dispersion of the heated coal in anthracene oil.

2. In the genetic series of coal with the same general origin (Kuznetsk basin), the degree of dispersibility in anthracene oil increases from the long-flaming coals to the fat coking coals and then drops off to the lean coals.

3. A high degree of dispersibility is manifested by a long-flaming, noncoking coal as well as by a good coking coal. Hence, characterizing a coal solely by determining its dispersibility in anthracene oil is not sufficient for determining the coking properties of a coal.

4. As coal is heated, its dispersibility, though remaining lower than for the original coal, remains constant throughout a certain temperature interval, then dropping off until this property disappears completely. This marks the conversion of the original coal into another state – semicoke, which is characterized by different chemical properties and a different structure of the bonds linking its elements together.

5. The order of sequence of the coals according to their dispersibility when heated is the same as for the original coals, fat coking coal being dispersed most readily and completely.

6. The rate at which the system condenses, marked by the decrease of the fraction dispersed in the anthracene oil, is a variable that is characteristic for each type of coal. All other conditions being equal, a high rate of condensation is displayed by gas and fat coking coals. The condensation of coals with a higher carbon content takes place over a wider temperature range and at a slower rate.

7. Comparison of the degree of dispersion, the rate of condensation, and the percentage of decomposition products enables us to get a clearer notion of the process involved in the formation of semicoke and with this to learn the reasons for the origin of the various qualitative indexes of coke.

8. It has been established that the noncoking, long-flame, "Zhurnik" coal can be dispersed under the proper conditions. The inability of this coal to yield a melted coke is due to its low content of substances that constitute the liquid phase when heated, its low thermal stability, and the direct decomposition of the coal into gaseous products, without passing through the stage in which stable liquid constituents are formed. As a result, the solid phase is not dispersed, and the coal does not enter the plastic state. These properties are occasioned by the high percentage of oxygen in the coal, which makes its organic material thermally unstable.

9. The coking capacity of a coal is related to its percentage of low-melting substances (soluble in alcoholic benzene) formed when it is heated. In good coking coals, the percentage of low-melting substances rises sharply as the coal is heated, being high even at low temperatures. In noncoking coals, the percentage of low-melting substances is low and does not increase as the temperature is raised.

10. The percentage of low-melting substances formed during the heating of coal is independent of the percentage of bitumen extracted from the original coal by alcoholic benzene.

LITERATURE CITED

[1] V.N.Novikov, Factory Lab., 5, 516 (1941).
[2] V.I.Zabavin, Bull. USSR Acad. Sci., Div. Tech.Sci., 4, 27 (1941).
[3] M.V.Gorftman, I.A.Kopelevich, and E.D.Kagan, Chemistry of Solid Fuels 6, 550 (1933).
[4] I.A.Kopelevich and E.D.Kagan, Chemistry of Solid Fuels 8, 703 (1935).
[5] S.A.Anurov and Ya.M.Obukhovsky. The Selection and Composition of Coal Charges in Coking, 30. Metallurgical Press (1940).

Received May 28, 1949.

RESEARCHES ON CINCHONA ALKALOIDS

N. E. Zeligson and V. V. Kolpakova

Analytical Laboratory, Sergo Ordzhonikidze All-Union Research Institute of Pharamceutical Chemistry

Separation and Determination of the Eight Principal Cinchona Alkaloids

A crystalline substance possessing antimalarial properties was first isolated from cinchona bark by the Portugese physician Gomez [1] in 1810; he called it cinchonine. In 1820, Pelletier and Caventou [2] secured cinchonine in purer form and in the same year they recovered quinine from cinchona bark.

Since that time numerous research workers have spent much time and effort on the isolation and study of the cinchona alkaloids, determining their composition and structure, and analyzing and synthesizing them.

There is a wealth of material available on the analysis of the cinchona alkaloids, in particular, summaries of this research being found in the textbooks by Bauer [3] and Korczynski [4]. After one goes through this material one cannot help coming to the conclusion that not one of the methods described is dependable or simple. These methods are based upon the peculiar reactions of the individual alkaloids, the properties of various salts of the individual alkaloids, and upon the differences in the solubility of the alkaloids themselves and of their salts in various solvents.

Separating the cinchona alkaloids on the basis of their solubility or that of their salts is rendered difficult, however, by the fact that cinchona alkaloids can form compounds that contain sparingly soluble alkaloids or their salts together with more readily soluble ones.

For example, quinine is readily soluble in ether, while cinchonidine is slightly soluble. But when an acid or neutral solution containing the salts of quinine and cinchonidine is agitated with ether and an excess of alkali, we do not get the crystals of pure cinchonidine, but those of a compound that contains 1 molecule of quinine and 2 molecules of cinchonidine. The sulfates constitute another example. Quinine sulfate is very slightly soluble in cold water (1:800 at 15°), whereas cinchonidine sulfate is much more soluble (1:98 at 15°). But it is extremely difficult to remove traces of cinchonidine from quinine sulfate by simply crystallization from water, not to mention quantitatively separating them.

The first method of separating and determining the four principal cinchona alkaloids (quinine, cinchonidine, quinidine, and cinchonine) was proposed by Hielbig [5]. His method was based upon the sparing solubility of quinine and cinchonidine tartrates in water, whereas the tartrates of quinidine and cinchonine

dissolve in water relatively readily. In the Hielbig method, 1.5-2 g of the alkaloid mixture is dissolved in an excess of dilute acetic acid, the solution is evaporated to dryness over a water bath, the residue is dissolved in water, the tarry substances that form (amorphous alkaloids) are filtered out, and the quinine and cinchonidine tartrates present in the filtrate (combined with the wash water) are precipitated with a Rochelle salt solution. The precipitated tartrates are suction filtered, washed with water, dried at 110°, and weighed. The filtrate and the wash waters are weighed in order to apply a later correction to the solubility of quinine and cinchonidine tartrates in water. The filtrate and the wash waters are evaporated to 20 ml, and 15 ml of alcohol and 0.5 g of sodium iodide are added. Quinidine hydriodide is thrown down; it is filtered out, washed with water, dried at 110°, and weighed. The conversion factor for converting quinidine hydriodide to free quinidine is 0.7171. The filtrate that remains after the separation of the quinidine is evaporated to remove the alcohol and then alkalinized with ammonia. The precipitated alkaloids are suction-filtered, washed with water, desiccated, and treated with 40-degree alcohol, which dissolves the other alkaloids (the residual quinine, cinchonidine, and amorphous alkaloids) but leaves the cinchonine undissolved. The latter is desiccated and weighed. Hielbig made use of the "herapathite" method previously developed by De Vrie to separate and determine the quinine and cinchonidine. This method is based upon the sparing solubility of herapathite,* quinine sulfate periodide, as compared to that of cinchonidine sulfate periodide [4].

The herapathite method is no longer used, because of its complexity and unreliability. The quinine and cinchonidine in a mixture of their tartrates are determined by measuring the specific rotatory power of the mixture and calculating the composition of the mixture from the specific rotatory power of quinine tartrate and cinchonidine tartrate.

Mention must also be made of the inaccuracy of the figures on the specific rotatory powers of the tartrates given in the Korczynski text [4].

He gives the specific rotatory power of the tartrates in a solution containing 0.4 g of the tartrate and 3 ml of a 1 N solution of hydrochloric acid per ml as:

Quinine tartrate $[\alpha]D - 215.8°$,
Cinchonidine tartrate $[\alpha]D - 131.3°$.

These figures have been taken from Oudemans [6] and refer to tartrates containing water of crystallization:

Quinine tartrate $2(C_{20}H_{24}O_2N_2)\cdot C_4H_6O_6 + H_2O$,
Cinchonidine tartrate $2(C_{19}H_{22}ON_2)\cdot C_4H_6O_6 + 2H_2O$.

Hille [7] used these figures directly (without correction) for the anhydrous salts. This error crept into Korczynski's text.

Zeligson has found the specific rotatory power of the anhydrous tartrates (at the concentration specified above) to be:

Quinine tartrate at 18° $[\alpha]D - 223.0°$,
Cinchonidine tartrate at 18° $[\alpha]D - 140.0°$.

The percentages of quinine tartrate (x) and of cinchonidine tartrate (y) are found from the following formulas:

$$x = \frac{[\alpha]D - (-140) \cdot 100}{-223 - (-140)} = \frac{([\alpha]D + 140) \cdot 100}{-83};$$

$$y = \frac{(-223 - [\alpha]D) \cdot 100}{-223 - (-140)} = \frac{(223 + [\alpha]D) \cdot 100}{83}.$$

*Named after Herapath who was the first to prepare it, in 1852.

The percentage of the tartrates found from these formulas is recomputed for the free bases, after which a further correction is made for the solubility of the tartrates in water. These corrections are fairly appreciable. 1 ml of water dissolves 0.000764 g of quinine tartrate and 0.000414 g of cinchonidine tartrate. The corrections for 30 ml of filtrate and 25 ml of wash water are:

	For the tartrates	Recomputed for the base
Quinine	0.0420	0.0341
Cinchonidine	0.0228	0.0182

The deficiencies of methods based upon the preparation of the tartrates are, on the one hand, the corrections that have to be applied, and, on the other, the lack of any allowance for the presence of hydro bases in the alkaloid mixture; of these hydro bases hydroquinine and hydrocinchonidine likewise form tartrates that are sparingly soluble in water. Hydroquinine is most commonly found together with quinine.

In 1935, Thron and Dirscherl [8] set forth the first group method for the quantitative separation of the principal cinchona alkaloids into vinylic and ethylic bases, founded on the ability of vinylic bases to add mercury, forming coordination compounds of the latter that are soluble in an excess of ammonia:

$$R > CH{-}CH{=}CH_2 + Hg(OH)_2 = R > CH{-}CH(HgOH){-}CH_2OH.$$

The ethylic cinchona alkaloids (the hydro bases) do not add mercury and can be extracted from the ammoniacal solution by an organic solvent. The mercury coordination compounds of the vinylic bases remaining in the ammoniacal solution are quantitatively converted into the original vinylic bases by acidulation with sulfuric acid followed by boiling with phosphorous acid. The sulfuric acid solution is acidulated with ammonia, and the vinylic bases are extracted with an organic solvent.

According to Thron and Dirscherl, the solution of the cinchona alkaloids in sulfuric acid is heated to 50° with a mercuric acetate solution for 4 hours.

We found that the addition of mercury is quantitative in the cold within 1.5 hours. We endeavored to rework Thron's and Dirscherl's method into a volumetric method for determining the vinylic bases by the consumption of mercury. We took a titrated solution of mercuric acetate and back-titrated the mercury that was not combined after mercuration of the vinylic bases against a solution of ammonium thiocyanate. The transition point proved to be unsharp, however, due, apparently, to the consumption of the ammonium thiocyanate to precipitate part of the complex bases.

The Thron and Dirscherl method has been worked out for the free bases, sulfates, and bisulfates, and is not applicable to salts of the cinchona alkaloids with other acids, which likewise form precipitates when reacted with mercuric oxide in ammonia. We have found a way of applying this method to any salt of the cinchona alkaloids without isolating the free bases in the dry state.

Separation of Vinylic and Ethylic Cinchona Alkaloids in Any of Their Salts

1 g of the salt of the cinchona alkaloids is dissolved in 15 ml of 1 N sulfuric acid in a separatory funnel; 25 ml of chloroform and 10 ml of a 10% solution of sodium hydroxide are added, and the whole is agitated. After the layers separate, the chloroform is drawn off into another separatory funnel, while the aqueous layer is again agitated with 15 ml and then with 10 ml of chloroform. The second and third chloroform extracts are combined with the first one and agitated with 10 ml of water. The chloroform is drained off into the first separatory funnel, which has been washed clean, the water being washed two times more with

5 ml of chloroform, which is again drained off into the same funnel. The combined chloroform solutions are agitated with 6 ml of a 10% solution of sulfuric acid, then 14 g of the Thron and Dirscherl solution (a 10% solution of mercuric acetate in a 5% solution of acetic acid) is added, and the whole is agitated again. The mixture is then set aside to stand for 4 hours at room temperature, being shaken from time to time. Then 10 ml of 10% ammonia is added, and the whole is shaken up again. The hydro bases enter the chloroform, while the vinylic bases remain in the ammoniacal solution as mercury coordination compounds. The rest of the analysis follows the Thron and Dirscherl specifications.

The method developed in 1940 by Zeligson and Sinkovskaya [9] for separating the principal cinchona alkaloids into those containing a methoxy group and those that do not is of the same group character.

In this method a mixture of the eight principal cinchona alkaloids is subjected to catalytic hydrogenation, yielding a mixture of four hydro bases: hydroquinine, hydroquinidine, hydrocinchonine, and hydrocinchonidine. The mixture of hydro bases is boiled with hydrobromic acid, as a result of which the hydroquinine and the hydroquinidine each lose a methyl group, being converted into hydrocupreine and hydrocupreidine, respectively, whereas hydrocinchonine and hydrocinchonidine remain unchanged. The solution is alkalinized with an excess of caustic soda, and the hydrocinchonine and hydrocinchonidine are extracted with an organic solvent. The hydrocupreine and the hydrocupreidine remain in the alkaline solution as phenolates.

By combining the Thron and Dirscherl method with the Zeligson and Sinkovskaya method, we can get a mixture of hydrocinchonine and hydrocinchonidine and a mixture of hydrocupreine and hydrocupreidine from vinylic as well as from ethylic alkaloids.

The methods of separating hydrocinchonine and hydrocinchonidine and separation hydrocupreine from hydrocupreidine are inadequate for the complete separation and determination of the eight principal cinchona alkaloids.

We know from the literature that the sulfates of cinchonine [10a] and hydrocinchonine [11] are soluble in chloroform. We tried to see whether hydrocinchonine could be separated from hydrocinchonidine by means of the different solubilities of their sulfates in chloroform, but we found that both sulfates were readily soluble in chloroform.

An optical method can be employed to determine hydrocinchonine and hydrocinchonidine; it yields fully dependable results, especially since the difference between the specific rotatory powers of these two alkaloids is very great.

We obtained the following results for an aqueous solution containing 0.1 mol of the alkaloid, 0.1 mol of hydrochloric acid, and 0.1 mol of sulfuric acid per liter: $[\alpha]D$ − 137.0° for hydrocinchonidine, and $[\alpha]D$ + 219.4° for hydrocinchonine. As for the separation and determination of the hydrocupreine and hydrocupreidine, we were unable to take up that problem for lack of quinidine, which is required for the preparation of hydrocupreidine.

Behavior of the Hydrochlorides of the Principal Cinchona Alkaloids in Organic Solvents

There are not many references in the literature to the solubility of the hydrochlorides of the principal cinchona alkaloids in organic solvents, and most of these references deal with the solubility of these salts in chloroform.

A mixture of 2 volumes of chloroform and 1 volume of 97-degree alcohol is a good solvent for the cinchona alkaloids and their salts. The extent to which

solubility in this mixture exceeds solubility in pure solvents is seen in the example cited by Hesse [12a]. Quinine sulfate dissolves in 1000 parts of chloroform and in 60 parts of 80-degree alcohol, whereas it dissolves in the proportion of 1:6 in the specified mixture of chloroform and alcohol. The hydrochloride [12b] and the oxalate [12c] of cinchonine are also freely soluble in this mixture.

Anhydrous cinchonine sulfate dissolves in 60 parts of cold chloroform and in 22 parts of boiling chloroform.[10a].

According to the literature the following hydrochlorides are soluble in chloroform: quinine [12d]; hydroquinidine [13]; hydrocinchonidine [10b]; and cinchonidine [14]. (When a solution of anhydrous cinchonidine hydrochloride in chloroform is allowed to stand in the cold for a long time, crystals containing about 20% of combined chloroform settle out. The crystals effloresce in air, losing chloroform).

We have found that the hydrochlorides of the other cinchona alkaloids are also readily soluble in chloroform. When an aqueous solution of a hydrochloride of a cinchona alkaloid is agitated with chloroform and sodium chloride, the hydrochloride salts out and reenters the chloroform solution.

As for the dihydrochlorides of the principal cinchona alkaloids, the only references in the literature are to the solubility of quinine and quinidine dihydrochlorides in chloroform [15]. According to Allen [10c], quinine dihydrochloride dissolves in 7 parts of chloroform, though Hager [16] asserts it is insoluble in chloroform. The French and Swiss pharmacopeias likewise mention the insolubility of quinine dihydrochloride in chloroform.

We have found that quinine dihydrochloride not only dissolves readily in chloroform, but even combines with chloroform to form unstable compounds of variable composition that contain water. They may be called solvates.

When an aqueous solution of quinine dihydrochloride is agitated with chloroform and sodium chloride and then allowed to stand, three layers separate out: the top one – a solution of sodium chloride containing very little quinine dihydrochloride; the bottom one – nearly pure chloroform, likewise containing only little of the dihydrochloride; and the middle one, containing almost all the quinine dihydrochloride.

This middle layer (the solvate) is thick and viscous, with a sp. gr. of about 1.25. The composition of the solvate is variable. In one case (I) it was equivalent to a compound of one molecule of quinine dihydrochloride with 4 molecules of chloroform and 3 molecules of water, while in another case (II) one molecule of the dihydrochloride was combined with 3 molecules of chloroform and 4 molecules of water (see Table).

A solvate may likewise be prepared from quinine disulfate by shaking up a solution of the latter with a saturated solution of sodium chloride and chloroform. This results in a double decomposition: the resulting quinine dihydrochloride combines with part of the chloroform, forming a solvate, while the sulfuric acid in the bisulfate enters the top aqueous layer as sodium sulfate:

$$Qu\cdot H_2SO_4 + 2NaCl = Qu\cdot 2HCl + Na_2SO_4.$$

The dihydrochlorides of other cinchona alkaloids that contain a methoxy group: hydroquinine, quinidine, and, most likely, hydroquinidine, can also form solvates. We were unable to check hydroquinidine in this respect, as the amount of quinidine at our disposal was too little to enable us to prepare hydroquinidine from it. The dihydrochlorides of the alkaloids containing no methoxy groups are insoluble in chloroform and yield no solvates.

Composition of Solvate I

Composition of solvate	Per cent found	Per cent computed for $Qu \cdot 2HCl + 4\ CHCl_3 + 3H_2O$
Quinine dihydrochloride	43.70	42.76
Water	6.07	5.81
Chloroform (as the difference).....	50.23	51.43

Composition of Solvate II

Composition of solvate	Per cent found	Per cent computed for $Qu \cdot 2HCl + 3CHCl_3 + 4H_2O$
Quinine dihydrochloride	48.22	48.00
Water	9.02	8.70
Chloroform (as the difference).....	42.76	43.30

We have found that solvates of the methoxy alkaloids can be prepared not only with chloroform, but with other organic solvents as well: dichloroethane, trichloroethylene, chlorotoluene, 2,4-dichlorotoluene, and carbon tetrachloride. But the arrangement of the layers may vary. For example, three layers are produced by quinine dihydrochloride, chlorotoluene (ortho and para mixture), and a saturated solution of sodium chloride: a lower layer – a solution of sodium chloride; a middle layer – the solvate; and an upper layer – chlorotoluene. With 1,2-dichloroethane, quinine dihydrochloride produces a solvate in the bottom layer, a saturated solution of sodium chloride in the middle layer, and dichloroethane in the top layer. The approximate composition of the solvate is $Qu \cdot 2HCl + 8H_2O + +C_2H_4Cl_2$:

	Found %	Computed %
$Qu \cdot 2HCl$	61.75	62.0
H_2O	21.34	22.5
$C_2H_4Cl_2$..... (as the difference)	16.91	15.5

When reacted with carbon tetrachloride, the solvate is found in the middle layer, as in the case of chloroform. This solvate is marked by an exceptionally high percentage of water and a low percentage of the organic solvent:

$Qu \cdot 2HCl$	61.50%
H_2O	30.24
CCl_4 ..... (as the difference)	8.26

A solvate may also be produced from a solution of quinine hydrobromide by agitating it with chloroform and a saturated solution of sodium bromide. The layers are arranged as follows: chloroform at the top, a saturated solution of sodium bromide at the bottom, and the solvate in the middle.

A solvate containing quinine dinitrate may be prepared by agitating quinine sulfate with chloroform and a saturated solution of sodium nitrate.

A New Method of Preparing Crystalline Quinine Dihydrochloride

The following methods are described in the literature for the preparation of quinine dihydrochloride: 1) the Liebig method [7] – passing gaseous hydrogen chloride over dry quinine; 2) the Hesse method [17] – evaporating a solution of quinine

dihydrochloride at "moderate" temperature: minute needles are precipitated at a "certain" temperature, but a jellylike mass is often obtained; 3) Carette [18] also prepared quinine dihydrochloride by evaporating its solution over a water bath and then allowing the solution to cool gradually; and 4) the Hager method [18] – dissolving 10 g of quinine hydrochloride in 25 ml of water and 3.7 g of 25% hydrochloric acid and letting it stand above calcium chloride until it crystallizes.

The preparation of quinine dihydrochloride is hampered by its extremely high solubility in water (1 part in 0.6 parts of cold water). As a result much of the quinine dihydrochloride remains in the mother liquor, while washing the crystals with water is out of the question. When they are washed with alcohol or with an alcohol-ether mixture, an oily layer of a concentrated aqueous solution of the dihydrochloride is recovered.

In our method the quinine dihydrochloride is prepared as follows:

The solvate of quinine dihydrochlorate with chloroform is mixed with half its volume of alcohol and two volumes of acetone are added. Acicular crystals of quinine dihydrochloride soon begin to precipitate. The next day they are filtered out and washed with acetone and ether. The wash liquid plus more ether are added to the mother liquor. This precipitates some more quinine dihydrochloride. The resulting quinine dihydrochloride possesses 3 molecules of crystallization water, two of which are given up at 50°.

It should be noted that the first crystallization contains a trace of sodium chloride. This is due to the fact that the middle layer contains suspended drops of the sodium chloride solution from the top layer, even after standing for a long time. The sodium chloride is not precipitated when alcohol is added to the solvate, and is precipitated together with the quinine dihydrochloride when the acetone is added.

This forced us to seek some way of producing quinine hydrochloride without using sodium chloride.

We see from the composition of the solvate of quinine dihydrochloride that the sodium chloride does not remove all the water from the aqueous solution of the dihydrochloride, leaving three to four molecules of water combined with the dihydrochloride and the chloroform as a solvate. But three molecules of water are required to produce the crystalline quinine dihydrochloride trihydrate.

The conversion of one gram molecule of anhydrous quinine hydrochloride into the dihydrochloride requires 94 g of hydrochloric acid, sp. gr. 1.19, containing 36.5 g HCl, and 57.5 g of water, or 3.3 gram molecules, i.e., about the quantity necessary for producing the solvate and recovering crystalline quinine dihydrochloride from it.

Ordinary quinine hydrochloride ($C_{20}H_{24}O_2N_2 \cdot HCl + 2H_2O$) need not be dried to dehydrate it. It is dehydrated with the same chloroform that is required for producing the solvate.

Production of crystalline quinine dihydrochloride. 100 g of quinine hydrochloride ($C_{20}H_{24}O_2N_2 \cdot HCl + 2H_2O$) is agitated with 200 ml of chloroform in a separatory funnel. After being allowed to stand, the chloroform solution is drained off into another separatory funnel, separating it from the layer of water that is formed. The computed quantity of hydrochloric acid, sp. gr. 1.19 (about 25 g), is added to the chloroform solution, and the whole is shaken together.

After the layers have separated, the lower chloroform layer is drained off. The residue in the separatory funnel (the solvate) is drained into an Erlenmeyer

flask and diluted with 75 ml of alcohol; then 400 ml of acetone is added. The next day the precipitated quinine dihydrochloride is suction filtered, washed with acetone and ether, and dried at 50°C.

SUMMARY

1. The eight principal cinchona alkaloids can be quantitatively separated only by means of group reactions:

a) In the Thron and Dirscherl method, the cinchona alkaloids are separated into vinylic and ethylic bases;

b) in the Zeligson and Sinkovskaya method, the alkaloids that do not contain a methoxy group are separated (as hydro bases) from the mixture of cinchona alkaloids.

The methoxy alkaloids are converted into hydrocupreine and hydrocupreidine. A combination of these two methods yields a mixture of hydrocinchonine and hydrocinchonidine and a mixture of hydrocupreine and hydrocupreidine.

2. The individual alkaloids in the hydrocinchonine – hydrocinchonidine mixture are determined by the specific rotatory power of the mixture.

3. The method of separating hydrocupreine from hydrocupreidine is not adequate for the complete separation and determination of the eight principal cinchona alkaloids.

4. The hydrochlorides of the principal cinchona alkaloids are readily soluble in chloroform.

5. The dihydrochlorides of the cinchona alkaloids that contain a methoxy group are soluble in chloroform and form thick solutions (solvates) with chloroform and a small amount of water, which are immiscible with an excess of chloroform and are decomposed by an excess of water.

6. Solvates are also produced with other organic solvents: dichloroethane, trichloroethylene, chlorotoluene, 2,4-dichlorotoluene, and carbon tetrachloride.

7. Dihydrochlorides of alkaloids that have no methoxy groups are insoluble in chloroform.

LITERATURE CITED

[1] Gomez. Ensaio sobre a cinchonino. Lisbon (1810); Memoria de Mathematica e Physica da Academia Real das Sciencias de Lisbon, III, 1, 202 (1812).

[2] Pelletiér et Caventou, Ann. chim., (2), 15, 291, 342, 348, 358 (1820).

[3] K.H.Bauer, Analytische Chemie der Alkaloide. 270-332 (1921).

[4] A. v.Korczynski. Die Methoden der exakten, quantitativen Bestimmung der Alkaloide. 24-45 (1913).

[5] C. Hielbig, Pharm. Z. f. Russland, 19, 289 (1880); Z. anal. Chem., 20, 144 (1881).

[6] A.C.Oudemans, Ann., 182, 67 (1876).

[7] W.Hille, Arch. Pharm., 241, 78 (1903).

[8] H.Thron und W. Dirscherl, Ann., 515, 252 (1935).

[9] N.E.Zeligson and A.K.Sinkovskaya, J.Gen.Chem., 15, 957 (1945).

[10] Allen's Commercial Organic Analysis, VII, a) 496, b) 494, c) 475.

[11] O. Hesse, Ann., 300, 53 (1898).

[12] O.Hesse, Ann., 176, a) 203, b) 230, c) 232, d) 210 (1875).
[13] M.Heidelberger and W.A.Jacobs, J. Am. Chem. Soc., 41, 826 (1919).
[14] O.Hesse, Ann., 176, 220 (1875).
[15] O.Hesse, Ann., 174, 341 (1874).
[16] Hager. Handbuch der pharmazeutischen Praxis.
[17] O.Hesse, Ann., 267, 143 (1891).
[18] H.Carette, J. Pharm. Chim., (6) 20, 347 (1904); (6) 22, 299 (1905).

Received December 15, 1950.

BRIEF COMMUNICATIONS

THE HYDROLYSIS OF 2,6,8-NAPHTHOLDISULFONIC ACID DURING THE SULFONATION OF β-NAPHTHOL

I. I. Vorontsov

Our preceding papers [1,2] demonstrated experimentally that the sulfo group at the 8 position in 2,8-naphtholsulfonic acid is hydrolyzed when beta naphthol is sulfonated with aqueous sulfuric acid. The second of these papers showed how the concentration of the sulfuric acid used for sulfonation affects the hydrolysis process.

As for the hydrolysis of the sulfo group in the 8 position in 2,6,8-naphtholdisulfonic acid, there have been no systematic investigations of this process as far as we can judge from the literature, though the existence of hydrolysis has been commented on more than once. Friedlander and Lucht [3], for instance, found that the action of sodium amalgam on a solution of 2,6,8-naphtholdisulfonic acid results in hydrolyzing the sulfo group in the 8 position. Shcherbachev [4] treated a solution of a salt of 2,6,8-naphtholdisulfonic acid with sodium amalgam and secured 2,6-naphtholsulfonic acid with a yield of 60-70% of the theoretical. In one of our papers [5] we have noted the hydrolysis of the sulfo group at the 8 position in 2,6,8-naphtholdisulfonic acid when beta naphthol is sulfonated with sodium polysulfate.

Inasmuch as the hydrolysis of the sulfo group at the 8 position in 2,6,8-naphtholdisulfonic acid is of theoretical interest and is, moreover, of considerable practical importance in view of the fact that this acid is always present in the production of an important intermediate for several sulfo acids of beta naphthol – 2,3,6-naphtholdisulfonic acid – we resolved to make a fuller study of the behavior of 2,6,8-naphtholdisulfonic acid when beta naphthol is sulfonated under conditions that favor the hydrolysis of the sulfo group at the 8 position.

EXPERIMENTAL

With this as our objective, we ran two series of tests with charges of 0.5 mol at a time, endeavoring to obtain as high an output as possible of 2,6,8-naphtholdisulfonic acid in the first series of tests, and then to set up the conditions that favor the hydrolysis of the sulfo group at the 8 position, i.e., to perform the sulfonation in two stages; in the second set of tests we performed the sulfonation from the outset under conditions that favored the hydrolysis process.

In the first set of tests the first stage of sulfonation was carried out in accordance with the well-known procedure for the synthesis of 2,6,8-naphtholdisulfonic acid [6], in which beta naphthol is sulfonated with the monohydrate or with weak (2-4%) oleum for 12 hours at 70-75°. Under these conditions, the sulfo mass contains 63-69% of the theoretical yield, i.e., close to the maximum possible,

of 2,6,8-naphtholdisulfonic acid with a relatively low percentage of 2,3,6,8-naphtholtrisulfonic acid [7].

After the first sulfonation stage was complete, various quantities of water were added to the sulfo mass, up to 10 mols per mol of the original sulfuric acid; the sulfo mass diluted with water was heated to 125° and stirred at 125-130° for 24 hours. Some tests were run without any water being added to the sulfo mass before heating. Samples of the sulfo mass were taken for analysis as follows: at the end of the first stage of sulfonation (before heating), then as soon as the temperature of the sulfo mass had reached 125°, and at intervals of half an hour for the first 6 hours and at intervals of 3 hours for the next 18 hours.

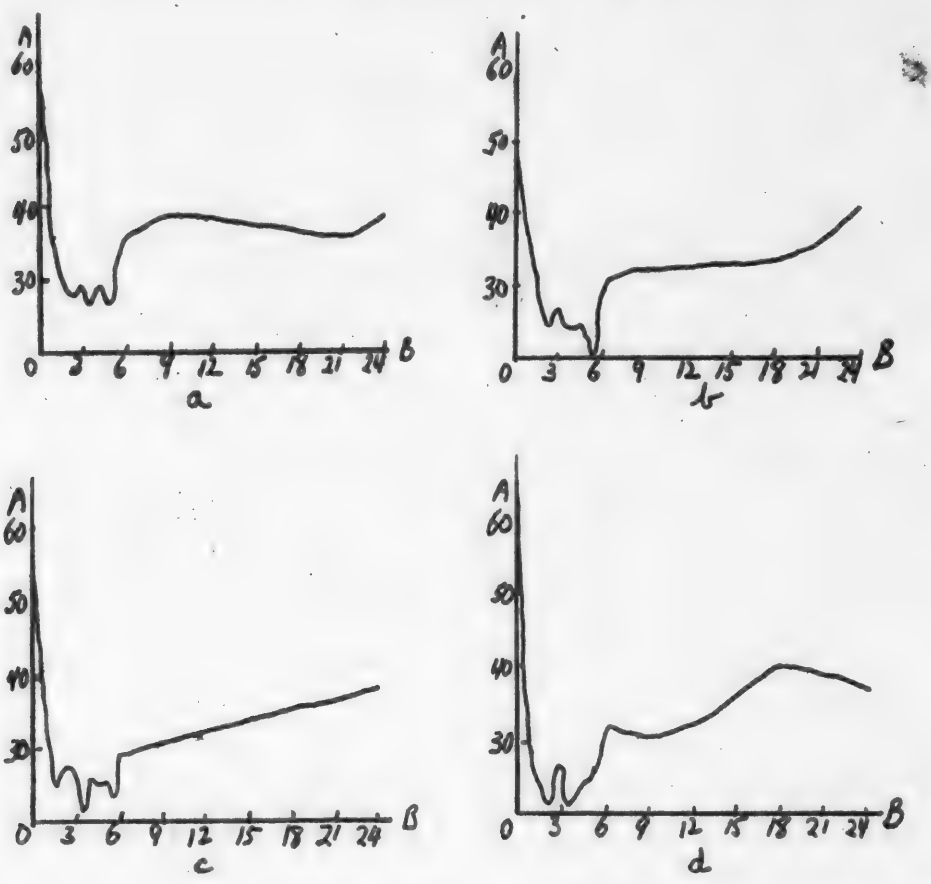


Fig. 1. Results of experiments on the sulfonation of beta naphthol with added water as a function of the time of heating of the sulfo mass. Temperature: 115-130°.

A-Percentage of slowly combining sulfo acids; B-time, hours. a-Test No. 13; b-Test No. 14; c-Test No. 15; d-Test No. 16.

Thus the number of analyzed samples of the sulfo mass totaled 20 for each test.

The following determinations were made in these sulfo samples: the total combining sulfo acids – by titrating with a solution of diazometanitrobenzene in soda; and the total quickly combining sulfo acids (i.e., the sulfo acids that have no sulfo group at the 8 position) – by titrating with a solution of diazo-

paratoluene in soda. With these analyses as a basis, the percentages of sulfo acids with a sulfo group at the 8 position, i.e., the total of the 2,6,8- and 2,3,6,8-naphtholdisulfonic acids, was calculated. The quantitative results of 4 tests run with and without adding various quantities of water to the sulfo mass are listed in Table 1 (in per cent of the total combining sulfo acids). The figures of Table 1 are plotted graphically in the diagrams of Fig. 1.

TABLE 1

Results of Tests of Hydrolyzing the Sulfo Group at the 8 Position

Time sample was taken for analysis	Sulfo acids with sulfo group at 8 position, as per cent of total combining sulfo acids			
	Water added to the sulfo mass, in mols per mol of H_2SO_4			
	0	0.4	0.8	1.2
	Test No.			
	13	14	15	16
Before heating	63.8	59.6	63.2	65.0
After heating to 125°	59.6	55.2	54.1	51.7
After stirring at 125-131° for 0.5 hour	50.8	44.4	42.9	33.3
1 hour	38.1	37.7	31.7	26.7
1.5 hours	31.1	31.7	24.1	24.6
2 hours	28.8	25.9	26.7	21.0
2.5 hours	27.6	24.6	27.1	25.9
3 hours	29.8	27.1	25.9	27.1
3.5 hours	26.3	24.2	21.1	21.1
4 hours	29.1	24.1	25.9	23.2
4.5 hours	29.1	25.0	25.0	25.0
5 hours	26.7	23.6	25.5	25.0
5.5 hours	32.0	20.4	23.1	28.6
6 hours	35.3	29.9	29.2	31.8
9 hours	38.5	32.0	30.6	30.6
12 hours	–	–	–	–
15 hours	–	–	–	–
18 hours	36.2	33.3	35.5	40.0
21 hours	35.3	35.3	43.1	44.6
24 hours	38.2	40.7	38.0	37.5

The table and the diagrams indicate the following:

1. As the temperature of the sulfo mass is raised from 70-75° to 125-130°, the hydrolysis of the sulfo group located at the 8 position in 2,6,8-naphtholdisulfonic acid sets in at once. This process is largely complete after 1.5 to 2 hours of stirring at 125-130°.

2. The sulfo group located at the 8 position is not completely hydrolyzed, since the per cent of 2,6,8-naptholdisulfonic acid remaining in the sulfo mass totals at least 20-25% of the total combining sulfo acids.

3. Adding as much as 1.2 mols of water per mol of charged sulfuric acid to the sulfo mass does not increase the hydrolysis of the sulfo group at the 8 position noticeably.

4. The percentage of slowly combining sulfo acids in the sulfo mass increases somewhat after 6 hours of stirring at 125-131°, apparently owing to the formation

Table 2. Results of tests sulfonating β-Naphthol under conditions that favor the hydrolysis of the sulfo group at the 8-position.

Sulfo acids determined	Yield of sulfo acids, per cent of the theoretical																	
	Length of sulfonation, hours																	
	0.5	0.5	1	1	2	2	4	4	6	6	12	12	18	18	30	30	42	42
2,8-Naphthol-sulfonic acid	13.0	11.4	9.6	11.6	8.2	7.6	4.2	4.6	0.8	1.2	0	0	0	0	0	0	0	0
2,7-Naphthol-sulfonic acid	10.2	10.2	9.4	8.8	6.4	6.8	5.2	5.2	4.6	4.4	3.4	3.6	3.6	3.4	2.8	3.2	2.6	2.4
2,6-Naphthol-sulfonic acid	60.4	61.8	56.8	55.6	47.2	47.2	38.8	38.8	36.4	38.4	30.2	31.4	18.6	19.0	13.8	13.4	7.6	7.6
2,6,8-Naphthol-disulfonic acid	8.4	9.2	18.2	11.6	15.2	16.0	24.0	22.0	24.4	23.6	22.6	23.8	22.8	22.8	22.0	22.2	23.8	22.4
2,3,6-Naphthol-disulfonic acid	8.0	7.0	11.0	12.0	23.0	22.0	27.0	29.0	33.0	32.0	43.0	40.0	55.0	54.0	59.0	58.0	60.8	62.0
2,3,6,8-Naphthol-trisulfonic acid	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.6	2.0	3.2	3.2
Sum total	100	99.6	100	99.6	100	99.6	99.2	99.6	99.2	99.6	99.2	98.8	100	99.2	99.2	98.8	98.0	97.6

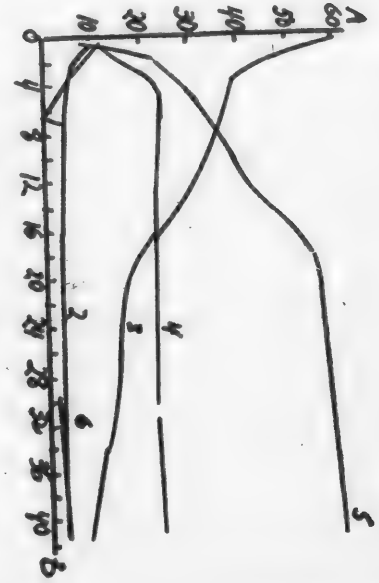


Fig. 2. Results of tests of the sulfonation of β-naphthol under conditions that favor hydrolysis of the sulfo group.

A – Yield of sulfo acids, % of theoretical;
B – Time, hours;
1 – 2,8-Naphtholsulfonic acid;
2 – 2,7-Naphtholsulfonic acid;
3 – 2,6 Naphtholsulfonic acid;
4 – 2,6,8-Naphtholdisulfonic acid;
5 – 2,3,6-Naphtholdisulfonic acid;
6 – 2,3,6,8-Naphtholtrisulfonic acid

of 2,3,6,8-naphtholtrisulfonic acid as the result of prolonged sulfonation.

Subsequent tests were run with the addition of water to the sulfo mass in quantities that ranged from 2 to 10 mols per mol of sulfuric acid. But in none of these tests were we able to lower the percentage of sulfo acids with sulfo groups at the 8 position below 20% of the total combining sulfo acids.

In the second set of tests the beta naphthol was sulfonated with 91% sulfuric acid, 2.67 mols of it being used per mol of beta naphthol, at a temperature of 100-105°, i.e., at the very outset the conditions favored the hydrolysis of the sulfo group at the 8 position. The duration of sulfonation was varied within very wide limits in the several tests – from 0.5 to 42 hours. All the tests of this series were run in pairs. In contrast to the tests in the first series, where the sulfo acids were determined in groups, in the second set of tests the following sulfo acids were determined individually: 2,8-, 2,7-, and 2,6-naphtholsulfonic acids; 2,6,8- and 2,3,6-naphtholdisulfonic acids; and 2,3,6,8-naphtholtrisulfonic acid. These acids were determined by the method suggested by Shcherbachev [4,8].

The quantitative results of these tests are listed in Table 2 (as per cent of the theoretical).

The diagram of Fig. 2 has been plotted from the data of Table 2 (using the mean of each pair of tests).

We see from Table 2 and the diagram that at the start the principal sulfonation product is 2,6-naphtholsulfonic acid, accompanied by approximately equal amounts of four "fellow-travelers": 2,8-, 2,7-, 2,6,8- and 2,3,6-sulfonic acids. But 6 hours after the start of sulfonation the picture changes markedly: almost all the 2,8-sulfo acid has vanished due to hydrolysis and sulfonation to 2,6,8-sulfo acid, while the percentages of 2,6- and 2,3,6-sulfo acids remain approximately the same. As sulfonation continues, the percentage of 2,3,6-naphtholdisulfonic acid gradually increases at the expense of the 2,6-sulfo acid, so that at the end of the period investigated by us most of the beta naphthol has been sulfonated to disulfo acids. 2,3,6,8-naphtholtrisulfonic acid appears in detectable quantities only after 30 hours of sulfonation.

As for the 2,6,8-naphtholdisulfonic acid, its yield reaches a maximum of 22-24% of the theoretical and remains at this level throughout the period we have investigated.

The next sulfonation tests were made at temperatures of 120-125° and 130-135°, in some of the tests 0.3 to 1.25 mols of water being added during sulfonation per mol of charged sulfuric acid. Nor were we able to reduce the percentage of sulfo acids with a sulfo group at the 8 position below 20% of the theoretical in these tests either.

SUMMARY

Our research has shown that no matter whether we start with a sulfo mixture containing the maximum possible quantity of 2,6,8-naphtholdisulfonic acid and perform sulfonation under conditions that favor the hydrolysis of the sulfo group located at the 8 position, or sulfonate beta naphthol from the outset under conditions that favor hydrolysis, we are unable to hydrolyze the sulfo group located at the 8 position completely. The minimum quantity of 2,6,8-naphtholdisulfonic acid that remains in the sulfo mass even under the most favorable conditions for hydrolysis totals 20-25% of the theoretical.

LITERATURE CITED

[1] I.I.Vorontsov, J. Appl. Chem. 13, 1470 (1940).

[2] I.I.Vorontsov, J. Appl. Chem. 21, 1002 (1948).

[3] P. Friedlander and Ph. Lucht, Ber., 26, 3028 (1893).

[4] K.D.Shcherbachev and A.E.Bashkirova. Aniline Dye Industry 4, 114 (1934).

[5] I.I.Vorontsov and P.N.Sokolova, Aniline Dye Industry, 4, 17 (1934).

[6] I.I.Vorontsov and P.N.Sokolova, Aniline Dye Industry, 5, 334 (1935).

[7] I.I.Vorontsov, J. Appl. Chem., 20, 464 (1947).

[8] K.D.Shcherbachev and A.Ya. Bashkirova, Aniline Dye Industry, 4, 206 (1934).

Received March 15, 1950.

THE YIELD OF DYESTUFFS IN COLOR DEVELOPMENT

A. N. Iordansky and G. I. Arbuzov

All-Union Institute of Cinema and Photographic Research

The method of producing movie films and photographic images on three-layer light-sensitive materials widely employed during recent years in the Soviet Union is based upon the use of color development using non-diffusing components that are introduced into the light-sensitive emulsion layers during manufacture.

The color image is formed at the same time as the exposed silver halide is reduced, by the reaction of the oxidation products of the developed substance, which is a derivative of p-phenylenediamine, with the undiffused components present in the emulsion layers being developed. The components employed in practice produce yellow, purple, and light-blue partial images in the several layers. The colors of these partial images meet the specifications of the general principles underlying multicolored images and provide a satisfactory color reproduction of the objects photographed.

The general form of the overall equation for the formation of dyes during color development is as follows [1]:

$$R_2'N \cdot C_6H_4 \cdot NH_2 + H_2CR''R''' + 4Ag^+ \rightarrow R_2'N \cdot C_6H_4 \cdot N{=}CR'R''' + 4Ag + 4H^+,$$

where R' is an alkyl group and R" and R"' are groups that impart mobility to the hydrogen in the methylene group.

Porai-Koshits [2] has shown experimentally that when a mixture of p-dialkylaminoanilines with α-naphthol (and its derivatives) or compounds containing an active methylene group is oxidized with silver bromide, the same dyes are formed as in the condensation of the respective nitro compounds with the same compounds, i.e., indoaniline and azomethin.

One of the present authors [3] has demonstrated that during the color development of the hidden photographic image, the p-aminodimethylaniline present in the emulsion layer forms an azomethin dye when 1-phenyl-3-methylpyrazolone is present, which is the same dye as is secured when a mixture of p-aminodimethylaniline and 1-phenyl-3-methylpyrazolone is oxidized by silver bromide.

The quantitative ratio of the dye formed during the reaction to the metallic silver was not established, however.

The concept put forward by Cheltsov of the relative dye output, expressed as the ratio of the increments of optical density $\Delta D\lambda/\Delta D_{Ag}$, where $D\lambda$ is the optical density of the dye as determined in the spectrophotometer at maximum absorption, and D_{Ag} is the corresponding optical density of the silver image, is a certain index to the magnitude of this ratio during the course of the process.

It is evident, however, that the ratio $\Delta D\lambda/\Delta D_{Ag}$ can express the relative

output of the dye only when no changes occur in the photometric equivalent of the reduced metallic silver in the gelatine layer, particularly when the same emulsion is used. The relative dye output is expressed by different figures for different emulsions, featuring different grain sizes of the silver halide (Table 1).

TABLE 1

Characteristics of Various Emulsions

Emulsion*	Mean radius of emulsion grain, μ	ΔD_{Ag}	ΔD_{520}	Relative dye yield
Negative I	0.40	0.4	2.60	6.5
Sound	0.35	0.4	2.25	5.6
Spectral	0.25	0.4	1.55	3.9
Negative II.....	0.31	0.4	1.67	4.2

The quantity that indicates the relative dye yield in color development also depends upon the way in which it is determined. If we determine the relative yield of the dye for constant exposure, varying the time of development, the shape of the $D_\lambda = f(D_{Ag})$ curve resembles somewhat the characteristic curve D_{Ag} as a function of log H (H being the amount of illumination). In the regions where D_λ and D_{Ag} are low or high, the ratio of their increments is a variable that reaches its maximum value along the straight-line portion of the curve. In the general case, this straight-line portion does not pass through the origin of coordinates.

We were interested in determining the ratio between the increments of the dye formed (ΔQ) and those of the metallic silver (ΔC), thus proving the equation set forth above for the formation of the dye. This ratio $\Delta Q/\Delta C$ may be called the true dye yield; it can be determined from the ratio $\Delta D_\lambda/\Delta D_{Ag}$ by finding the relationship between ΔQ and ΔD_λ on the one hand, and ΔC and ΔD_{Ag} on the other.

Nor was finding the relationship between the dye yield and the mean size of the silver halide grains in the emulsion less interesting. It could be assumed that a change in the mean size of the grains of silver bromide in the various emulsions used in manufacturing would affect the yield of the dye during color development.

EXPERIMENTAL

We determined the dye yield by selecting emulsions with various sizes of the grains of the silver halide. These emulsions and the mean radii of their emulsion grains as determined by us are listed in Table 1.

We selected a purple dye specially prepared from the same component used in the emulsion to coat the photographic layers, in our determination of the relationship between the optical density of a dye and the quantity present.

We then prepared 5% solutions of gelatin containing various amounts of the purple dye. These solutions were used to prepare dry gelatin films, and the optical densities of these films were measured at $\lambda = 520$ mμ (maximum light absorption for the purple dye). The amounts of the dye, in mols per cm^2 of surface, and the respective optical densities are listed in Table 2.

The optical density of the color layers produced as a function of the surface concentration of the purple dye is shown in Fig. 1. It is represented by a straight line that passes through the origin. Hence, the purple dye introduced into the gelatin film obeys Beer's law, at least at optical densities ranging from 0.00 to 3.00. By analogy with the photometric equivalent of the developed metallic silver, the quantity of dye in grams (g) per cm^2 of surface, for an optical

*The first three emulsions are of the ammonium type, while Negative II is a nonammonia emulsion.

density of 1 at the absorption maximum of $D_{520} = 1$ may be termed the photometric equivalent of the developed color layer, i.e.,

$$\underline{q} = \frac{Q}{D_{520}},$$

where q is the amount of dye per 1 cm^2 of surface.

In our case, the photometric equivalent of the color layer, $\underline{q}' = 2.65 \cdot 10^{-8}$ mol per cm^2, expressed in mols of dye per cm^2 at $D_{520} = 1$ (Fig. 1).

TABLE 2

Optical Density of the Dye as a Function of the Quantity Present

Quantity of purple dye, mols/cm^2	Optical density at $\lambda = 520\mu$ (D_{520})
$0.74 \cdot 10^{-8}$	0.27
$1.48 \cdot 10^{-8}$	0.52
$2.96 \cdot 10^{-8}$	1.07
$5.91 \cdot 10^{-8}$	2.16
$8.87 \cdot 10^{-8}$	3.44

When we compare the complete absorption curve for the pure purple dye introduced into the gelatin film (Curve II, Fig. 2) with that for the dye produced by the color development of the exposed photographic film containing undiffused components (Curve I), we find they coincide satisfactorily. We may, therefore, conclude that the dye introduced into the gelatin film is in the same physical state as the dye formed as the result of color development.

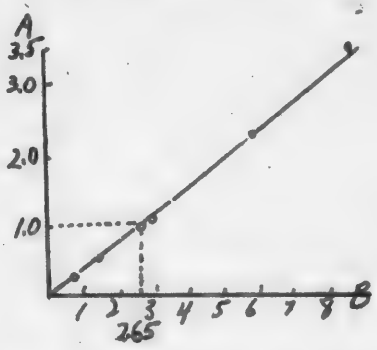


Fig. 1. Variations of the optical density D_{520} of the colored layers with the quantity of purple dye present per cm^2

A-Optical density D_{520}; B-quantity of the purple dye, Q, mols/cm·10^{-8}.

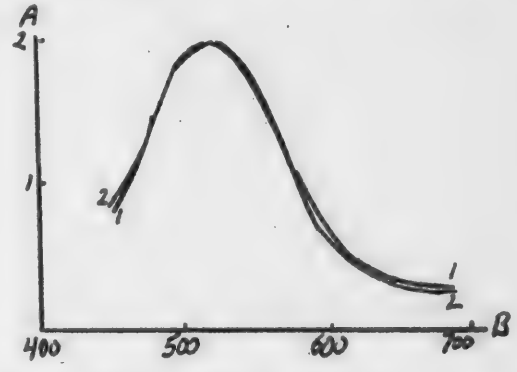


Fig. 2. Curves of the spectral absorption of purple dyes.

A-Optical density; B-wavelength, μ. 1-Dye produced by color development; 2-Purple dye introduced into the gelatine film.

In all the emulsions tested, the proportions of the silver bromide, gelatin, and the color component were kept constant prior to the preparation of the light-sensitive films in order to eliminate any variation of the dye output with a change in these proportions. The emulsions were not sensitized, in order to simplify the investigation. The quantity of emulsion applied was the same in all the tests (5 ml of emulsion per 108 cm^2). After the coating had dried, the resultant photographic films were given constant exposures. The exposed plates were developed for varying periods of time (ranging from 0.5 to 3.5 minutes) in a color developer of constant composition. The resulting sensitograms were cut in half longitudinally, the silver densities being determined in one half, and the color densities in the other. The dye was bleached out by treating the film with a solution of dilute sulfuric acid in order to determine the D_{Ag}; the silver was removed by successively treating the film with potassium ferricyanide and sodium thiosulfate to make determination of the D_{520} possible.

The relative dye yield was determined for the straight-line portion of the

$D_{520} = f(D_{Ag})$ curve at densities of the silver image ranging from 0.2 to 0.6, i.e., $\Delta D_{Ag} = 0.6 - 0.2 = 0.4$. The difference between the values of the optical density ΔD_{520} for the range of silver densities $\Delta D_{Ag} = 0.4$ (within the limits 0.6 and 0.2), as well as the values of the relative dye yields for various emulsions are given in Table 1.

The photometric equivalents were determined for the tested emulsions. These quantities, expressed in grams as well as in gram atoms (p') of silver per cm^2 of surface for $D_{Ag} = 1$, are listed in Table 3. The true dye output may be computed from the formula:

$$\varphi = \frac{\Delta Q}{\Delta C},$$

where $\Delta Q = q' \cdot \Delta D_{520}$ and $\Delta C = p' \cdot \Delta D_{Ag}$, on the basis of these values of the photometric equivalents of the developed silver images and color images.

TABLE 3

Photometric Equivalents of Emulsions Tested

Emulsion	Photometric equivalent of reduced metallic silver	
	Grams Ag/cm^2 (p)	Gram atoms Ag/cm^2 (p')
Negative I.	$7.5 \cdot 10^{-5}$	$6.95 \cdot 10^{-7}$
Sound.....	$6.2 \cdot 10^{-5}$	$5.75 \cdot 10^{-7}$
Spectral...	$4.6 \cdot 10^{-5}$	$4.26 \cdot 10^{-7}$
Negative II	$5.0 \cdot 10^{-5}$	$4.63 \cdot 10^{-7}$

The results of these calculations are given in Table 4. Table 5 gives the values of the relative and true dye yields, as well as the mean radii of the emulsion grains.

TABLE 4

True Dye Yield for Various Emulsions

Emulsion	Silver				Purple dye		True dye yield, $\varphi = \frac{\Delta Q}{\Delta C}$
	ΔD_{Ag}	p'	ΔC	ΔD_{520}	q'	ΔQ	
Negative I.	0.4	$6.95 \cdot 10^{-7}$	$2.78 \cdot 10^{-7}$	2.6	$2.65 \cdot 10^{-8}$	$6.92 \cdot 10^{-8}$	0.248
Sound	0.4	$5.75 \cdot 10^{-7}$	$2.30 \cdot 10^{-7}$	2.25	$2.65 \cdot 10^{-8}$	$5.99 \cdot 10^{-8}$	0.260
Spectral...	0.4	$4.26 \cdot 10^{-7}$	$1.70 \cdot 10^{-7}$	1.55	$2.65 \cdot 10^{-8}$	$4.12 \cdot 10^{-8}$	0.242
Negative II	0.4	$4.63 \cdot 10^{-7}$	$1.85 \cdot 10^{-7}$	1.67	$2.65 \cdot 10^{-8}$	$4.44 \cdot 10^{-8}$	0.250

The overall equation for the reaction involving the formation of a dye during color development, cited above, gives the dye yield as 0.25 mol per gram atom of silver.

The yield of the purple dye found experimentally was 0.240-0.260 mol of dye per gram atom of silver.

TABLE 5

Data on the Mean Radius of the Emulsion Grains and the Dye Yield, Relative and True, for Various Emulsions

Emulsion	Mean radius of emulsion grains, μ	Relative dye yield	True dye yield
Negative I.	0.40	6.5	0.248
Sound	0.35	5.6	0.260
Spectral...	0.25	3.9	0.242
Negative II	0.31	4.2	0.240

SUMMARY

1. It has been shown experimentally that during color development purple dye is formed at the rate of 1 mol per 4 gram atoms of reduced metallic silver,

which bears out the theoretical concepts of the formation of dyes during this process.

2. It has been shown that for emulsions in actual use the true dye yield is unaffected by the mean size of the emulsion grains.

LITERATURE CITED

[1] A.G.Tull, Brit. J. Phot., 86, 115 (1939).

[2] A.E.Porai-Koshits, Bull. USSR Acad. Sci., Div. Chem. Sci., 3, 261 (1945).

[3] G.I.Arbuzov, J. Appl. Chem., 23, 8 (1950).

Received January 30, 1950.